MOVEMENT AND TRANSFORMATIONS OF UREA-N IN THREE FOREST SOILS OF THE SOUTHEASTERN COASTAL PLAIN

By

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1974

DEDICATED

TO THE MEMORY OF

MY BELOVED MOTHER

ACKNOWLEDGMENTS

I sincerely thank Dr. William L. Pritchett and Dr. Wayne H. Smith for acting as Cairman and Co-chairman, respectively, of the Supervisory Committee, for helping develop the problem, for their constructive criticisms during the preparation of this dissertation, and for their overall guidance and support throughout the study. I also thank Luther C. Hammond and Dr. Robert S. Mansell for their valuable suggestions on the soil physical aspects of the problem. Special thanks are due to Dr. Jonn A. Cornell for his guidance in the statistical analysis of the data.

I heartily extend appreciation to the following: (1) the Cooperative Research in Forest Fertilization (CRIFF) program for financial support, (2) Mrs. Mary C. McLeod for her valuable help in the laboratory, (3) Dr. Herman L. Breland, Mrs. Helen A. Brasfield, and Miss Emma V. del Mundo for the mineral analysis, (4) Dr. Russell Ballard, Mr. Roylin L. Voss, and Mr. James B. Emmons for their help and brotherly companionship, (5) Mr. James W. Gooding for helping facilitate computer analysis of the data and his friendship, and (6) Mrs. Paulita R. Puzon for typing this dissertation.

To the light of my life, Nattie, I owe a world for her understanding, painstaking sacrifice during moments of crisis, help in the collection and preparation of the experimental materials and laboratory work, and patience in typing the draft of this dissertation. A special appreciation to Edzel and Glenn for being a constant source of "inspirational distractions."

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Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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December, 1974

Chairman: Dr. W. L. Pritchett
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A series of lysimeter, greenhouse, and laboratory experiments were conducted to determine the influence of soil moisture, soil organic matter and clay content, and rates of urea application on the transformation and movement of urea in forest soils. It was hoped that the results of these tests would help characterize the transformation pathways of urea-N applied to Southeastern Coastal Plain forest soils possessing various characteristics.

High rates of ureolysis and ammonification were observed when soil moisture conditions were maintained within the range of 0 to 170 cm of soil water tension. When the soil matric suction was allowed to reach 345 to 1000 cm of water, about 8 to 50 % of the added urea-N remained in its unhydrolyzed form at the end of 42 days. About 8 to 18 % of the added urea-N was lost due to volatilization of ammonia when the soil matric suction was allowed to reach 500 cm of water. Ammonification was observed to be the predominant conversion pathway of urea-N. Nitrification was generally low under all conditions tested. Urea fertilization invariably increased soil pH.

Rates of ureolysis and ammonification were faster in Plummer fs with 20 % organic matter than in Leon fs or Bladen sl with 0.92 and 2.75 % organic matter, respectively. Phenylmercuric acetate was more effective as a urease inhibitor in the Leon fs than in the Plummer fs.

Urea fertilization caused a decrease in the non-extractable N component of the soil, indicating an increased rate of mineralization of the organic N fractions. The amounts of non-extractable N decreased from 93 to 65 %, 98 to 77 %, and 97 to 92 % of the total initial N content in the Leon fs, Bladen sl, and Plummer fs, respectively. The degree of decomposition of the soil organic matter components appeared to be the main factor affecting the urea fertilization-N mineralization relationships.

Urea appeared to be a better fertilizer than ammonium sulfate for two-year-old slash pine, particularly under high soil moisture conditions. Favorable growth response to urea fertilization was probably due to a temporary rise in soil pH which may have favored better nutrient availability, increased metabolic efficiency resulting from an increased supply of ammonium ions, the possible uptake of unhydrolyzed urea and the products of ureolysis such as ammonia and carbonates, and minimized leaching losses of nutrients. Poor growth response to ammonium sulfate was probably due to high concentrations of soluble salts and high leaching losses of nutrients. An accounting of the N distribution in the lysimeter experiment showed that urea and ammonium sulfate fertilization resulted in slash pine uptake of 64 and 49 %, leaching losses of 17 and 51 %, and apparent gaseous losses of 19 and 0 % of the added N, respectively.

INTRODUCTION

Steadily increasing demand for wood products and ever decreasing land areas available for expanded commercial timber production have led to the use of forest fertilization as one of the intensive forest management tools to increase wood production per unit land area. Although forest fertilization has been practiced in some countries for over 70 years (Tamm, 1968), it only has been during the last decade that forest fertilization has gained recognition as an effective silvicultural method to increase tree growth.

In the Southeastern United States, results from field experiments undertaken by the Cooperative Research in Forest Fertilization (CRIFF) program have indicated that about 2 million hectares (ha) of 12- to 16-year-old pine plantation, 310,000 ha of pines planted yearly, and another 310,000 ha of existing plantation that will annually reach an age of 12 to 16 years are responsive to both nitrogen (N) and phosphorus (P) fertilization (CRIFF ANNUAL REPORT, 1973). Considering positive indications that a large percentage of these potentially responsive areas will be fertilized, it is reasonable to expect that about 60,000 to 80,000 tons of N will be used annually in the future.

There are over 2000 grades of fertilizer containing N (Hauck, 1968) but only a few formulations have been commonly utilized as N sources, particularly in forest situations. One of these N carriers is urea. This fertilizer has been widely used in stimulating the

growth of established and newly planted forest stands in many countries. Results have been so encouraging that forest fertilization operations in Sweden (Tamm, 1968), Japan (Mitsui, 1967), Canada (Roberge et al., 1970), the Pacific Northwestern USA (Norris and Moore, 1971), and the Southeastern USA (CRIFF ANNUAL REPORT, 1973) have included urea as an N source. These, among other developments such as those associated with agronomic practices, have greatly stimulated increased production of urea at such levels that justify the claim that the future of the fertilizer N supply market belongs to urea (Harre and Mahan, 1973).

Several favorable attributes have led to the wide acceptance of urea as a forest fertilizer. These are (1) high N concentration (45 % to 46 %), (2) low leachability after conversion to ammonium (NH_4), (3) capacity to temporarily raise the pH of acidic soils, (4) low potential for ground water contamination with nitrates, (5) non-combustible or explosive, (6) low corrosive properties that lend to easy and low-cost handling, and (7) blends well with other fertilizer materials.

However, there are some problems that tend to negate the effective and efficient use of urea in forest ecosystems. After urea is added to forest soil-plant systems, microbial and humus immobilization, volatilization, denitrification, leaching, and injury to seedlings may cause problems.

Particular forest situations determine whether to use urea for a given forest ecosystem. Thus, it is necessary to characterize and understand the transformation pathways the fertilizer undergoes under the influence of the prevailing forest site factors. The primary concern of this study was the movement and transformations of urea-N

in forest soils. The objectives were to (1) study the movement and transformations of urea as affected by soil type, soil moisture regimes, and levels of N application, and (2) determine the effects of urea and ammonium sulfate [$(NH_4)_2SO_4$] fertilization on growth response of potted slash pine, soil pH, and residual soil N.

LITERATURE REVIEW

The Use of N in Forest Fertilization

Comprehensive reviews on worldwide forest fertilization were compiled by White and Leaf (1957), Stoeckeler and Arneman (1960), and Baule and Fricker (1970). Progress and potential of forest fertilization in North America have been reviewed by Gessel (1968), Beaton and Tisdale (1969), Roberge et al. (1970), and Weetman and Hill (1973). The potential for forest fertilization in the Southeastern Coastal Plain of USA was recently reviewed by Pritchett and Smith (1970).

Experimental results indicating favorable growth response of different tree species to N fertilization are well documented (Gessel and Walker, 1956; Baule and Fricker, 1970; Weetman and Hill, 1973). Despite the widespread deficiencies of N in most soils, N fertilization of forests have not always produced positive responses. Several experiments with N fertilization of planted pine seedlings resulted in poor growth response (Hughes and Jackson, 1962; Pritchett and Llewellyn, 1966; Pritchett, 1972). Several factors have been considered responsible for such poor response: high solubility and rapid leaching of most N fertilizer, high salt index, stimulation of weeds which compete with the tree seedlings for nutrients or water, suppression of mychorrhizal development at high N levels, improper fertilizer placement, and poor timing of fertilizer application (Austin and Strand, 1960; Pritchett and Robertson, 1960; Bengtson and Voigt, 1962; Richards and Wilson, 1963).

The above factors suggest that the solution to the effective use of N fertilizers may be in choosing the proper application of the correct N source. Different tree species have different silvical characteristics and soil types widely vary in their physical and chemical properties. These factors plus climatic conditions and biological influences affect the rate of N conversion, utilization, and losses. However, the problem of choosing the proper N source may be simplified by the fact that coniferous trees generally respond to ammoniacal sources and that in acid forest soil, nitrification is generally slow (Smith, et al., 1971).

Urea in Forest Fertilization

Urea is the N fertilizer most commonly used to stimulate growth of established stands in several countries. In Sweden, economical returns from forest fertilization trials with urea led to large-scale application of urea, particularly by the Swedish Cellulose Company (Hagner, 1966; Tamm, 1968). Favorable results of experiments conducted and compiled by the Ministry of Agriculture and Forestry in Japan have resulted in this country becoming one of the leading manufacturers and users of urea (Mitsui, 1967). Stagnating black spruce stands in the boreal forests of Canada showed significant growth stimulation from a combined treatment of thinning and urea fertilization (Roberge et al., 1970). The authors attributed the favorable growth response to the mobilization of N contained in the thick humus accumulated on the forest floor. In the Pacific Northwestern USA, major commercial coniferous timber types have responded to N fertilization, regardless of source (Norris and Moore, 1971; Cochran, 1973). But because of its high N content and adaptability

to aerial application, urea has been the main source of N for operational fertilization in this region. Urea is also the recommended N source for the operational fertilization of N responsive sites in the Southeastern Coastal Plain of the USA (CRIFF Annual Report, 1973).

There are several reasons behind the wide acceptance of urea as a forest fertilizer. Urea is the most concentrated (45 % to 46 % N) dry N source available and this makes it superior to other sources in terms of handling cost per unit N weight. This is especially significant in forest fertilization operations which usually cover vast area of land with considerable tonnages of fertilizer materials.

Although highly soluble in water, urea is more resistant to leaching than NH_4NO_3 (Garn, 1973). Leaching of unhydrolyzed urea is believed to be retarded by certain mechanisms associated with the clay and organic matter contents of the soil (Chin and Kroontje, 1962; Broadbent and Lewis, 1964; Mitsui, 1967; Ogner, 1972). Under suitable conditions following addition of urea to acid forest soils, ammonification is the predominant transformation pathway. This is particularly significant in the acid flatwoods sites of the Southeastern USA where slash pine (Pinus elliottii Engelm. var. elliottii) is one of the important native species that grow well with NH_4 as the predominant N form (Smith, 1972; personal communication). Since nitrification in this region is in most cases negligible following urea fertilization of acid forest soils (Pritchett and Smith, 1970; Smith et al., 1971) the potential for polluting ground water with nitrates is minimal.

Upon ureolysis, urea causes soil pH to rise (Kresge and Satchell, 1960; Fiedler, 1971; Beaton, 1973). In the microsites immediately surrounding the fertilizer granules, pH may reach 11.0 (Fiskell, 1972;

personal communication). Although this pH rise is temporary, it may be beneficial to acid forest soils in terms of enhanced availability of nutrients (Beaton, 1973).

By virtue of its non-combustible, non-explosive, and less hygroscopic (when uncontaminated) properties, urea appears to be a fertilizer material suitable for long-term storage, safe in transport via low-cost water transportation, and possessing excellent blending ability with other fertilizer materials.

The extensive use of urea, however, is somewhat hindered by highly variable and often unsatisfactory growth response of fertilized forest trees. Fiedler (1971) showed that in several cases, calcium nitrate [$Ca(NO_3)_2$] and ammonium sulfate [$(NH_4)_2SO_4$] were 5 to 60 % better than urea in terms of tree growth response. For example, in Quebec, Canada dry matter production of pine and spruce for two growing seasons was about 50 % less with urea fertilization than with $Ca(NO_3)_2$ or $(NH_4)_2SO_4$ applications. Diameter growth of a 50-year old spruce stand in East Germany was increased by 30 % with $Ca(NO_3)_2$ but only by 13 % with urea. In Sweden, average growth response of coniferous stands to urea has been reported to be nearly 35 % lower than the growth response to NH_4NO_3 (Nommik, 1973b).

Urea may also be less effective than other N sources on other crops. For example, Power (1974) reviewed the effects of urea fertilization on grassland productivity and found that at application rates higher than 90 kg/ha, NH_4NO_3 is 8 % to 12 % better than urea. A greenhouse study on the fertilization of orchardgrass in Washington (Klock et al., 1971) found that $(NH_4)_2SO_4$ elicited greater dry weight response than urea. The authors attributed the difference in response to sulfur

(S) deficiency of the plants. There may be some influence due to soil pH which ranged from 5.2 to 6.1.

The reported superiority of $Ca(NO_3)_2$ to urea could be partly due to the effect of Ca on acidic forest soils. However, other processes are certainly associated with the superiority of NH_4NO_3 and $(NH_4)_2SO_4$ to urea. These processes may include immobilization, volatilization, denitrification, leaching, and injury to plants.

Immobilization

Several reports indicate that substantial amounts of urea-N added to forest soils are immobilized by microbial cells and humus. After reviewing the work of Huser (1969), Fiedler (1971) reported that 10 to 20 % of added urea may be used in the construction of microbial tissues and up to 20 % in the formation of stable humus compounds. Overrein (1970) reported higher values of immobilized N obtained after incubating urea-treated raw humus. After 60 days of incubation at 12 C, 71 % of the urea-N added at the rate of 50 ppm was in the non-mineralized form; about 8 % of which was KCl-extractable. At a higher incubation temperature (20 C), maximum immobilization (75 %) occurred with the 100 ppm treatment and only 4 % was KCl-extractable. The relationship between urea-N application rate and temperature vis-a-vis maximum immobilization indicates microbial action.

Although microbial immobilization may be high, this N form may become available subsequent to the death and decomposition of microbial tissues. However, the organic N forms may be held in stable humus complexes and rendered unavailable for plant uptake over sustained periods. Furthermore, the re-mineralized N may be gradually incorporated in the non-extractable fraction of humus N (Overrein, 1970, 1972b).

The above process of immobilization probably occurs following the

hydrolysis of urea. There are reports that indicate immobilization of urea in its molecular form. Chin and Kroontje (1962) postulated that the formation of relatively stable urea-organic matter complexes resulted from physical or chemical adsorption and was primarily related to soil organic matter content. Subsequent investigations appeared to confirm this hypothesis. Broadbent and Lewis (1964) obtained data from a series of chromatographic elution that indicated the ability of urea to form salts with carboxylic groups of soil organic acids. Using mercuric chloride (HgCl) to inhibit urease activity, Mitsui, (1967) found that over a concentration range of 0.01 to 1.00 M the adsorption of urea by volcanic ash soil was linear while that of $(NH_4)_2SO_4$ peaked at 0.10 M. It was also found that volcanic ash and peat soils had higher capacities to adsorb urea (46 and 42 mg of urea-N per 100 g soil, respectively) than coarser soils or soils with lower organic matter content. Based on these data and some spectrographic evidence, Mitsui (1967) postulated that the main mechanisms of urea adsorption by soils is the formation of hydrogen (H) bonds with the carboxylic (-COOH), carbonyl (-C=O), and phenolic (C_6H_6-OH) groups of soil organic acids.

Ogner (1972) sutdied the effects of urea fertilization on raw humus collected under spruce and Scots pine stands in Norway. Through proximate analysis method of N extraction and organic matter fractionation, he obtained quantitative and spectrographic evidence of urea-N incorporation in the humus matrix. Reactions with -COOH, -C=O, and C_6H_6OH groups were the mechanisms considered responsible for such incorporation. Furthermore, Ogner cited the possibility of re-synthesis of hydrolyzed urea-N upon reaction with the polymeric groups of soil

organic compounds. Hubert (1974, personal communication) stated that urea-N incorporation by humic compounds is a result of the fact that N is a structural part of the non-hydrolyzable heterocyclic organic compounds that form through polymerization.

It would appear that the main mechanism of humus immobilization of urea is associated with its ability to self polymerize (Mitsui, 1967) or polymerize with the decomposition products of organic matter (Ogner, 1972). Said (1972) reported that soil adsorption of unhydrolyzed urea was not related to organic matter content of the soil. It may be pointed out, however, that the soils used in the latter study had low organic matter contents (0.41 to 2.22 %). It is possible that within the usual range of organic matter contents of soils, there is a critical organic matter percentage at which reactions postulated by Mitsui (1967) and Ogner (1972) would start to operate. Salt formation with soil organic acids (Broadbent and Lewis, 1964) may contribute to the retention of unhydrolyzed urea by soils or may be a key step towards polymerization reactions. Unless urea becomes part of the unhydrolyzable heterocyclic organic compounds of the soil or is associated with clay adsorption mechanisms, salt formation appears to be a short-term mechanism of urea retention in the soil.

Volatilization

When urea is added to the soil, the volatilization pathway may predominate, especially when its application is made improperly or conditions conducive to volatilization occur. Kresge and Satchell (1960), Allison (1964), Gasser (1964), Bengtson (1970), Fiedler (1971), and Watkins et al. (1972) reviewed the volatilization losses of ammonia (NH_3) from urea added to agricultural soils. Losses as high as 50 %

of the added N were reported. In general, high volatilization losses were found to be associated with the following: (1) surface application to bare soils, (2) calcareous soils or soils made so by liming, (3) soils of low cation capacity (CEC), (4) soils of low buffering capacity, (5) low soil moisture conditions (losses are especially high during the drying cycle following the wetting of the soil), (6) high soil temperature, (7) high wind speed, and (8) high urease activity. Results from studies with agricultural soils cannot necessarily be used to predict volatilization losses from forest soils. Gaseous losses of ammonia (NH_3) from acid forest soils are usually considered low (Beaton, 1973). This appears to be borne out by the results of several investigators. Overrein (1969) fertilized highly acidic podzolic forest soil in Norway with urea-N at rates of 100, 250, 500, and 1000 kg/ha. Maximum volatilization loss was only 3.5 % of the added N over a period of 48 days. Application of 672 kg/ha of urea-N in similar podzolic soils in Newfoundland resulted in negligible gaseous losses of NH_3 and a rise in pH of only 0.4 to 0.5 unit (Bhure, 1970). On a strongly acid fine sand under a natural slash pine stand in Florida, Volk (1970) found volatilization losses of 4 % in 7 days following surface application of 100 kg/ha of urea-N. Volk also found losses of 2 % from an area that had been control-burned 5 weeks before fertilization and 5 % from an area bared of loose debris.

On the other hand, other studies indicated much greater losses of gaseous NH_3. Fiedler (1971) reported that volatile losses resulting from the fertilization with urea of a sandy soil under a jack pine stand amounted to 15 % of the 112 kg/ha of the added N. He also reported that losses increased with increasing rates of application.

In laboratory studies in which forest soils obtained from Douglas-fir stands were held at different moisture and pH levels, Baker (1970) detected up to 21 % of volatile losses from 448 kg/ha of urea-N added. In Baker's study, soil pH increased to about 8 regardless of the initial value, and volatile losses were decreased by lowering the temperature from 13 C to 5 C and the soil moisture content to below 10 %. It was also observed that bringing the soil moisture content to 150 to 300 % delayed gaseous losses of NH_3.

Watkins et al. (1972) studied the effects of air flow rates, temperature, and pH on volatilization of NH_3 from urea applied to forest soils taken as undisturbed cores from Douglas-fir, western hemlock, and sitka spruce stands in the Pacific Northwest. Their results showed that at an air flow rate equivalent to 10 m/hr and temperature of 19 C, NH_3 losses ranged from 6 to 30 % of the 224 kg/ha of urea-N surface applied to bare mineral soils and 27 to 46 % for the same application rates to forest floor surfaces.

Nommik (1973a) assessed NH_3 losses from N^{15}-labelled urea applied to vertically isolated microplots (24.5cm in diameter and 15 cm deep) under a 90-year old Scots pine stand. Evolved NH_3 was not directly monitored but indirectly determined from the difference between the N added and the N recovered in the soil profile. Results showed that after 13 days of exposure, gaseous NH_3 losses were 25 % from small pellet-size urea and 12 % from tabletted (2.06 g/tablet) urea. For a 31-day exposure, unrecovered N was 27 % from the pellet-size and 15 % from the tabletted urea.

The differences in the magnitude of volatilization losses reported by various investigators may reflect the various factors

affecting volatilization. However, experimental procedures also may be of importance. In certain studies, NH_3 evolved is monitored by allowing a sweep of air to pass across the soil surface under air-tight enclosure. This method favors removal of NH_3 by mass flow which may not necessarily occur under field conditions. Other methods rely on diffusion of gaseous NH_3 into acidified sorbers. This system may develop positive pressure relative to the soil air pressure such that volatilization may be unrealistically retarded. The most reliable method of assessing volatilization losses appears to be the one employed by Nommik (1973a) which determines evolved NH_3 from the difference between N added and N recovered in the soil profile. This method, however, requires labelled material and plant uptake accounting.

To minimize NH_3 losses through volatilization, Allison (1964) and Volk (1970) recommended that urea fertilizer should be mixed with the soil. In forestry practices, however, it is not economical nor practical to apply and incorporate fertilizer in such vast areas involving considerable tonnages of fertilizer in stands often inaccessible to ground equipment. Furthermore, when fertilization is done in young stands where tree roots are already extensive, mechanically mixing the fertilizer with the soil may damage the roots making them subject to Fomes annosus infection. Thus, alternative means of minimizing NH_3 losses and improving the efficiency of urea as a fertilizer are needed. Characterizing the soil and environmental conditions that favor the transformation pathways of urea to the extent that N availability is optimized may provide such alternatives.

Denitrification

Denitrification is an N transformation pathway which returns

mostly molecular and nitrous oxide forms of N (N_2 and N_2O, respectively) to the air. Sites may suffer N deficits if this process predominates in the N cycle. Alexander (1961) stated that except in fields populated with legumes, a condition that often leads to N accretion, N deficits are the rule.

Several examples of soil N depletion brought about by denitrification and the conditions responsible for such losses were given by Bremner and Shaw (1958), Alexander (1961), Carter and Allison (1961), Allison (1963), Meek and Mackienzie (1965), and Borishova and Zertsalov (1966). Denitrification losses ranging from 6 to 73 % of the added N have been reported. In general, denitrification requires a (1) good supply of decomposable organic compounds to serve as proton donors and energy source, (2) high nitrite (NO_2) or nitrate (NO_3) levels to serve as terminal proton acceptors, (3) poor drainage in which microbial oxygen demand exceeds supply, (4) high acidity which regulates the supply of protons, and (5) high temperature (within the range of optimum biological activity).

In certain cases, denitrification may occur following the addition of urea to forest soils. Upon complete ureolysis, subsequent reactions may lead to the production of hydroxyl (OH) ions and nitrification. In the first case, high pH may develop, especially at the microsites immediately surrounding the urea granules. Such processes affect nitrification by forcing the oxidation of NH_4 to terminate at the NO_2 form. This could happen because the microorganisms (Nitrosomonas) responsible for the production of NO_2 are less inhibited by high pH than those (Nitrobacter) responsible for NO_3 formation (Alexander, 1961; Fiedler, 1971). Martin et al. (1943) stated that pH 7.7 is the threshold value beyond which NO_2 could no longer be converted to NO_3.

In this situation, decomposing organic matter (enhanced by urea fertilization may protonate the accumulating NO_2 (more easily than the NO_3 form) to produce water and N_2 or N_2O. Accumulating NO_2 may, however, diffuse out of the highly alkaline pocket and be further oxidized to NO_3 (Olson el al., 1971).

The soil pH optimum for nitrification is 8.5, but it can occur over a pH range of 5.5 to 10.0 (Tisdale and Nelson, 1966). Nitrification is known to take place in a few agricultural soils at pH as low as 3.8 but in forest soils, it may practically cease below pH 5 (Beaton, 1973). Because forest soils have existed for a long time at such low pH levels that nitrifying organisms are nearly absent or rendered ineffective (Pritchett and Smith, 1970; Smith et al., 1971), nitrification in untreated acid forest soils is generally considered to be of minor importance.

Cases of considerable nitrification, however, have resulted from urea fertilization of forest soils, especially at high rates of N. For instance, Roberge and Knowles (1966) found that over an incubation period of 42 days, NO_3 production in highly acidic humus (pH 3.3 to 4.7) treated with 3,500 ppm of urea-N went as high as 15 % of the added N. Overrein (1971) recovered 50 % of the added N as NO_3 oever 40 months following the fertilization of forest soils (in lysimeter systems) with 1,000 kg/ha of urea-N. In the Southeastern USA, Smith et al. (1971) obtained a maximum nitrification rate of 25 % during 24 weeks of incubation of acid sandy soils treated with 90 to 180 kg/ha of urea-N.

It must be pointed out that the above data were obtained from incubation studies or soil profiles enclosed in lysimeters. Both systems may operate under conditions not found in nature. Despite the claim of Overrein (1969) that processes involving accumulation and evolution

of N_2O and N_2 are not operative in relatively well aerated and highly acidic forest soils, the above data would indicate the possibility that urea-fertilized forest soils may produce considerable NO_3 which may be enzymatically or chemically reduced to N_2O or N_2.

Leaching

The ability of forest soils to restrict nutrient movement has long been recognized (Joffe, 1933; Hardy, 1936; Ovington, 1960). However, the intensified use of N in forest fertilization during the last decade and the rising concern on environmental quality have led to the recognition of N leaching losses as a problem of sufficient importance to justify extensive research.

There are three general methods that have been used in assessing leaching losses from the soil: lysimetry (filled-in or monolith), stream sampling from gaged watersheds, and suction cup sampling.

Lysimeter studies are advantageous in that they often incur less expense, generate quick results, facilitate replications (Hornbeck and Pierce, 1973), and allow more complicated experimental designs. However, results from lysimeter studies can not be readily applied to natural conditions. Use of disturbed soil profiles, development of unnatural water regimes, and consequently abnormal nutrient movements in lysimeter soil make interpretation of results difficult. Use of tension-plates at lysimeter bottoms may reduce some of these shortcomings (Cole, 1958), but variations in leachate volumes through tension-plate lysimeters (Cochran, 1970) may make quantification of leached nutrients difficult. Furthermore, Nutter and Ike (1970) pointed out that lysimeters can only sample discrete sections of the hydrologic continuum from stream to ridgetop. Despite the shortcomings of lysimeters, the method is still

a very useful approach to studying nutrient movements, transforamtions, and budgets.

Sampling streams draining from gaged watersheds can overcome some of the above shortcomings. The approach incurs less problems with interpretation of results because it integrates all the variables that influence nutrient leaching (Nelson, 1970). Furthermore, the use of gages facilitate quantification of data. The main disadvantages of the gaged watershed method are that the system is not flexible to replications and complicated experimental designs and it involves considerable expense and elaborate organization of personnel (Hornbeck and Pierce, 1973).

The use of suction cup samplers is a relatively new system of collecting soil solution. Quantification is not possible with this system, which is its main disadvantage. But it can facilitate immediate detection of nutrient concentration changes at or near the sites of chemical reactions or biological activities, which may not be accounted for by the gaged watershed method. There seems to be no one perfect system of assessing leaching losses of nutrients but the above may be combined to obtain maximum results.

Broadbent et al. (1958) determined the comparative leachability of urea and other NH_4-bearing fertilizers through 22-cm laboratory columns. They found that urea moved more readily than the other fertilizer materials. More recent investigations tend to contradict these results. Using lysimeters equipped with tension-plates about 90 cm below the surface, Cole and Gessel (1965) found very small leaching losses after applications of urea or $(NH_4)_2SO_4$ to a Douglas fir stand in the Pacific Northwest. Fiedler (1971) reviewed the study of Huser (1971) and found that

urea was less leachable than NH_4NO_3 and that losses were greater from coarse than fine textured soils. A lysimeter study carried out by Overrein (1969) on a podzolic forest soil in Norway showed that leaching losses of N from lysimeters fertilized with urea, ammonium chloride (NH_4Cl), and potassium nitrate (KNO_3) were 15, 100, and 300 times greater than the losses from unfertilized plots. Nommik and Popovic (1971), using laterally isolated microplots in a Scots pine stand in Sweden, showed that urea had much slower mobility than either $Ca(NO_3)_2$ or $(NH_4)_2SO_4$. A lysimeter study in Canada indicated leaching losses of less than 1 kg/ha of urea-N applied to a black spruce stand (Roberge et al., 1971).

The differences in the findings of Broadbent et al. (1958) and the other investigators may be resolved in terms of leaching depth and the time leaching occurred. Broadbent et al. (1958) monitored their leachates to a depth of 22 cm, 1 to 24 hours after application. Cole and Gessel (1965), Overrein (1969), and Nommik and Popovic (1971) determined leaching to depths of 90, 45, and 40 cm, respectively, and their leaching times varied from weeks to months. The difference in space and time may have allowed sufficient opportunity for urea to react with the soil or the humus fraction, which consequently minimized leaching.

Tamm and Wiklander (1971) investigated the effects of N fertilization on ground water and streams draining Swedish coniferous forests. Their results showed that stream water concentrations of NO_3-N and NH_4-N were 8.6 ppm and 5.9 ppm, respectively. They concluded that fertilizing forests with urea would pose no danger of polluting the ground water or streams provided the fertilizer is not directly spread over water courses. In another study, Friburg (1971) applied 112 kg/ha of urea-N around the perimeter of a forest lake in Sweden. In the first summer after treatment, N concentration in the lake went up to 0.6 to

0.8 ppm and went down to 0.2 to 0.5 ppm in the second summer.

Moore (1970) reported that fertilization of Douglas-fir in southwestern Oregon with 224 kg/ha of urea-N caused stream concentrations in urea, NH_4, and NO_3 to increase only slightly above background values. All forms of N had returned to pre-treatment levels by the fourth week after application. Aerial urea fertilization of two forested creeks in Washington caused urea concentration to increase on the day of application; NO_3 levels increased to a maximum of 1.32 ppm one week after fertilization and was back to pre-treatment levels after 4 months (McCall, 1970).

Klock (1971) studied the effects of urea fertilization of burned watersheds in north central Washington. At 60 days after fertilization, 1.37 kg of urea-N and 2.90 kg of NO_3-N were estimated to have been carried by streamflow from the watershed receiving 27,500 kg of urea-N. The maximum concentrations detected were 0.6 ppm and 0.2 ppm for urea and NO_3-N, respectively.

Aerial application of 115 kg/ha of urea-N to a young hardwood forest in West Virginia (Aubertin et al., 1973) yielded results somewhat different from the above. During the first growing and dormant seasons after fertilization, 17.4 % of the added N was carried in the stream discharge as NO_3-N. Maximum stream concentration of NO_3-N reached as high as 19.8 ppm, which was generated by a high storm flow. A study on the effects of fertilizing young slash pine plantations with different forms fo N on groundwater quality was undertaken by the CRIFF program at the University of Florida, Gainesville (CRIFF unpublished data). Peak N concentrations in the water samples were detected 20 days after fertilization, as shown below:

N treatment		Leachate concentrations	
Source	Rate (kg/ha)	NH_4-N (ppm)	NO_3-N (ppm)
Control	0	0.30	1.40
Urea	90	4.40	0.30
Ureaform	90	1.20	2.60
$NaNO_3$	90	0.60	50.00
$(NH_4)_2SO_4$	90	11.90	1.40
NH_4NO_3	90	4.65	2.00

Concentration of NO_3-N in samples of collected from sites treated with NH_4NO_3 peaked again at 14.2 ppm 37 days after fertilization, while those collected from urea-treated sites peaked at 6.2 ppm 50 days after fertilization. The above data indicate that, in terms of total NH_4-N plus NO_3-N movement, urea is the least leachable of the N sources tested.

Concern has been commonly expressed on N leaching losses as NO_3-N. This concern undoubtedly stems from the fact that most soils have a low anion exchange capacity making nitrates easily leached, unless denitrification or biological uptake takes place. Leaching losses of N as NH_4-N may also occur when the soil exchange sites are temporarily overloaded or when the soil is inherently low in CEC Thomas, 1970). Leaching of NH_4-N may be further enhanced if, after applying NH_4-bearing or NH_4-converting fertilizers, negligible nitrification occurs, plant or microbial uptake is slow, and soil water percolation is rapid. This was substantiated by the findings of Aubertin et al. (1973) which indicated that urea fertilization increased the NH_4-N concentration of stream water for 5 weeks before

it returned to its original level. The data shown in the above table indicate that NH_4-N is the main form of N involved in leaching losses of urea.

Urea may be leached in its unhydrolyzed form. The solubility of urea in water, its chemical or physical neutrality, and its low dissociation constant (1.5×10^{-14} at 25 C) are attributes that make this fertilizer susceptible to leaching in its unhydrolyzed form. Klock (1971), Norris and Moore (1971), Aubertin et al. (1973), and Tiedemann (1973) detected unhydrolyzed urea-N in stream water samples. However, they claimed that most of the amounts detected were attributable to wildlife excretion. It would appear that unhydrolyzed urea-N is not an important form of leaching losses of N, especially if precipitation occurs after fertilization to effect rapid infiltration and complete ureolysis. Leadhing of unhydrolyzed urea may also be retarded by mechanisms associated with the soil organic matter and clay contents (Chin and Kroontje, 1962).

Injury to Plants

Urea has a salt index of 1.62 (Tisdale and Nelson, 1966). It may be harmful to plants by the formation of biuret contaminants, production of free NH_3, and by accumulations of NO_2.

Biuret contaminants, formed from 2 molecules of urea during its synthesis and processing especially at high temperature, have been formed in urea solutions heated to more than 50 C (Gasser, 1964). Biuret toxicity has been mostly observed on germinating seeds and leaves receiving foliar spray of urea solution. Several cases of biuret toxicity were reviewed by Gasser (1964). However, it appears that this problem has diminished in importance because present manu-

facturing technology is capable of minimizing biuret formation in the factory (Philipps, 1973).

The free NH_3 that is produced during or after ureolysis may be harmful if absorbed by the roots in toxic amounts. Damage to agricultural crops by NH_3 injury has been fairly common as indicated by the reviews of Gasser (1964) and Viets (1965). Mesa (1974) recently observed that tomato seeds were prevented from germinating, or germinating seedlings failed to survive, due to urea application to an alkaline soil. Soil pH rises subsequent to ureolysis may be such that activities of Nitrobacters are inhibited. This would result in NO_2 accumulation and toxicity. Court et al. (1962) described cases of crop damage due to NO_2 accumulation. Passioura and Wetselaar (1972) studied the effects of N fertilizer salts on wheat roots. They found that $(NH_4)_2SO_4$ restricted root growth via increase in osmotic potential of the soil solution. This effect lasted for 4 weeks. On the other hand, urea more severly inhibited root growth by generating high NO_2 concentrations (maximum of 100 ppm) and the toxic effects persisted for 8 weeks. Accumulation of NO_2 was likely in that experiment because of high initial soil pH (6.7 to 7.8).

Urea also had been observed to cause injury to nursery grown slash pine seedlings which were transplanted to an acid flatwoods soil (pH 4.3) in the Southeastern USA (Smith et al., 1971). Seedling survivals in pots fertilized with urea were lower than those fertilized with NH_4NO_3 and ureaform, and survival decreased with increasing N applications rates. Lowest survival resulted from urea-N application of 448 kg/ha. Ammonia toxicity generated during or after ureolysis was probably responsible for such low survival.

Potential damage owing to urea fertilization is most important in forest nursery operations where seedlings are more susceptible to either salt injury or toxicity due to accumulation of free NH_3 and NO_2. Cases of fir and pine seedlings being damaged by soluble N fertilizers, one of which is urea, were reviewed by Smith et al. (1971).

SUMMARY

From the foregoing reviews of research on the transformations of urea in soils, a number of problems are brought into focus. These problems involving the effective use of urea appear to be influenced by the following conditions:

1. If water is added too soon after application, there may be a flushing of the fertilizer out of the root zone.
2. If watering is delayed, conditions may favor high volatilization rate.
3. If adequate water is added at the proper time, microbial and humus immobilization may prevail.
4. If organic matter is high, volatilization or immobilization may result.
5. If organic matter is low, volatilization and/or leaching may prevail.
6. If temperature is high, rapid rate of volatilization is very likely to prevail; if temperature is low, ureolytic activity may not be sufficient for a rapid rate of conversion of the fertilizer into its ionic forms.

To avoid the above kind of dilemma, it is important that the transformation pathways and the complete spectrum of reactions consequent to the application of urea to forest soils be thoroughly understood.

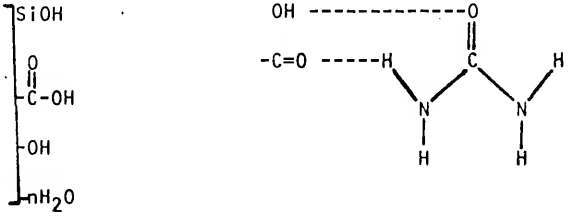
Overall Fates and Reactions of Urea

The cycling of N in forest ecosystems is an important nutritional and environmental factor. Urea plays an important role in this cycling because of the varied transformation pathways it undergoes in the soil-plant system. The role of urea in the overall N cycling may be complicated by the fact that even in its unhydrolyzed form, it may get immobilized, leached, adsorbed on clays, absorbed by roots, and hydrolyzed (Fig. 1).

Clay Adsorption

Said (1972) found that soil adsorption of unhydrolyzed urea was highly correlated with CEC and clay content. It was also demonstrated by Mitsui (1967) that urea moved much slower in soils with high clay content than coarser textured soils. Gasser (1964) found that urea was adsorbed by sodium (Na), magnesium (Mg), calcium (Ca), barium (Ba), and aluminum (Al), and montmorillonites. Furthermore, Pearson et al. (1962) observed that when urea was applied to soils, Ca and Mg move downwards less than when $(NH_4)_2SO_4$ was applied.

Clay adsorption of urea may involve H-bonding, polyvalent cations, ligand exchange, water bridges, and soil organic compounds. McLean and Peterson (1965) and Mitsui (1967) postulated that urea may form H-bonds with some radicals associated with clay colloids as shown below:



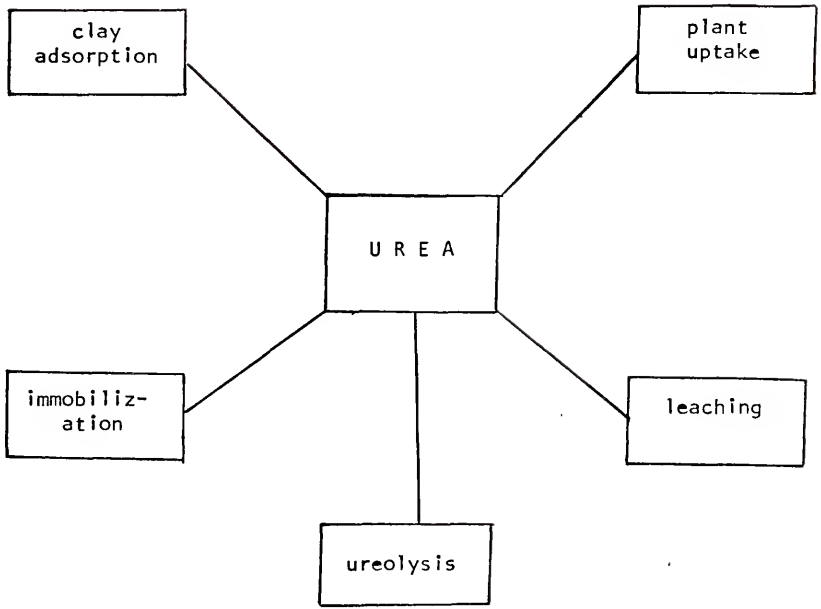


Fig. 1. The fates of urea

The amide groups may also react with cations in the same manner as amines because the former are readily adsorbed in the cationic forms by exchange for inorganic ions (Greenland, 1965).

Polyvalent cations act as bridges between clay and organic compounds (Greenland, 1965). It has been pointed out earlier that urea may be a polymeric component of certain humus structures. If such organic compounds linked to clay edges via polyvalent cation bridges carry urea molecules, immobilization of urea more stable than humus immobilization would occur. Stability of this type of reaction may be maintained because proteins, which predominate in organic matter, attached to clay edges or lattices are resistant to microbial attack (Greenland, 1965).

Soil organic compounds are adsorbed on clays, particularly kaolinite, through ligand exchange (Greenland, 1971). In this type of adsorption, the organic anion ($R\text{-}COO^-$, for example) penetrates the coordination shell of an iron (Fe) or aluminum (Al) atom in the hydroxide surface, thus affecting incorporation of the anion with the surface hydroxyl layer. Urea incorporation in this manner may be achieved by virtue of its slightly electronegative property which can stimulate the production of organic anions or by being a structural part of organic anions.

Clay adsorption of uncharged organic compounds is weak (Greenland, 1956). But uncharged polymers are adsorbed strongly and in large amounts (Emerson, 1963). Furthermore, Emerson (1963) also reported that once uncharged polymers are adsorbed on clays, they are extremely difficult to desorb. It would appear, therefore, that polymerized urea compounds (Mitsui, 1967) and polymeric urea-humus structures may

adsorb on clay with considerable stability. From a plant nutrition standpoint, direct clay adsorption of urea is more desirable than humus complexation or adsorption through ligand bridges because in the former urea may be made available through CEC reactions,

Plant Uptake

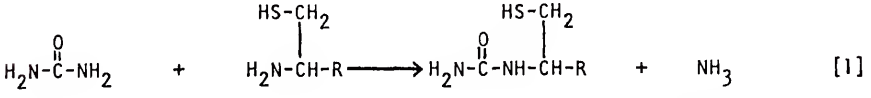
Studies on absorption, movement, and decomposition of urea in plants suggest that the compound is absorbed both by roots and leaves and moves intact until hydrolyzed at the points of growth Gasser (1964), Although beneficial effects of urea on plant growth through foliar uptake are well documented (Gasser, 1964; Tisdale and Nelson, 1966; Pritchett and Eberhardt, 1972), less information on direct root uptake is available. Most detections of absorption of unhydrolyzed urea were made on cereals, particularly wheat and rice (Mitsui, 1967), Because of the rapid hydrolysis to NH_4-N in most soils, Tisdale and Nelson (1966) believed that direct root absorption of unhydrolyzed urea is a minor occurence. Several reports indicated that directly absorbed unhydrolyzed urea would be hydrolyzed inside the plant and that the NH_3 produced would be utilized in the synthesis of proteins (Mitsui, 1967). However, the same source indicated that urea could be absorbed by plants with no urease and the urea incorporated in protein compounds without recourse to the NH_3 form. The postulated mechanism of urea assimilation in this manner is the reverse reactions of the ornithine cycle.

Direct uptake of unhydrolyzed urea may be beneficial because (1) it can supply the plant with N even without the benefit of hydrolysis, (2) it can supply plants with carbon without requiring some photosynthetic steps, (3) urea may be incorporated with the protein

compounds or amino acids with fewer physiological steps, (4) danger of damage due to NH_3 or NO_2 toxicity may be averted, (5) it may provide the primary means of N uptake from urea immobilized in humus structures or adsorbed on clays, and (6) it can provide plants with N supply under conditions unfavorable for rapid ureolysis. Durzan (1973) studied the metabolic pathway of ^{14}C-urea in 15-day-old spruce seedlings and found that urea provided carbon (C) for the synthesis of allantoic acid and carbamyl phosphate. He also found that urea served as a cofactor in the synthesis of pyruvic acid and, through urease, provided C for the synthesis of numerous sugars and organic acids.

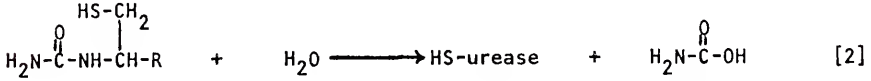
Ureolysis

Ureolysis is the conversion of molecular urea to ammonium carbonate [$(NH_4)_2CO_3$] through the action of H_2O and urease. A series of chemical reactions are involved in this process. Some of the reactions were given by Sumner (1951).



(urea) (HS-urease) (urea-urease) (ammonia) [1]

In Eq. [1], one amide ($-NH_2$) is removed, picks up a proton from sulfhydryl urease (HS-urease), and forms NH_3. Blakely et al. (1969) and Sundaram and Laidler (1970) showed that carbamic acid (NH_2COOH) is the first product of ureolysis. In the presence of H_2O, the urea-urease complex is hydrolyzed. This results in the release of the HS-urease as it regains its proton from H_2O and the formation of NH_2COOH. This process is shown in Eq. [2].



(carbamic acid) [2]

Sumner (1951) did not show the reactions necessary to carry out the conversion of urea to $(NH_4)_2CO_3$. It is probable that the following reactions represent the necessary intermediate steps according to Hart and Schuetz (1972) and Manziek (1974, personal communication):

$$H_2N\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \quad + \quad NH_3 \rightleftharpoons H_2N\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^-NH_4^+ \qquad [3]$$

The NH_3 formed in Eq. [1] provides the electronegative force to remove a proton from NH_2COOH with the consequent formation of NH_4^+ and carbamate (NH_2COO^-) ions which then neutralize each other through ionic bonding. The remaining $-NH_2$ of the original urea molecule may then be deaminated as in Eq. [1] and, by undergoing the same reactions as in Eqs. [2] and [3], $(NH_4)_2CO_3$ is formed.

Eq. [3] is a reversible reaction and indirectly influences the fate of the NH_3 produced in Eq. [1]. If, instead of reacting with NH_3, NH_2COOH reacts with some other nucleophiles, NH_3 may be lost through volatilization unless it finds another proton source in the soil solution system. However, since these two reactants share common source and site of reaction, proximity would increase the likelihood of the reaction in Eq. [3]. Furthermore, NH_3 is an efficient nucleophile (Hart and Schuetz, 1972). The rate of Eq. [3] reactions would then be dependent on the rate of NH_3 and NH_2COOH production on the one hand and $(NH_4)_2CO_3$ accumulation on the other.

Sumner (1951) reported two kinds of urease: HS-urease and hydroxyl urease (HO-urease). These two enzyme species differ from each other only in terms of reaction sites as Eqs. [1] and [4] would show.

$$H_2N\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \quad + \quad \underset{\text{(HO-urease)}}{\overset{HO\text{-}CH_2}{\overset{|}{H_2N\text{-}CH\text{-}R}}} \longrightarrow \underset{\text{(urea-urease)}}{H_2N\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-urease}} \quad + \quad NH_3 \qquad [4]$$

As in Eq. [2], hydrolysis of the urea-urease complex would result in HO-urease regaining a proton from H_2O and the formation of NH_2COOH.

Consequences of Ureolysis

Ammonium carbonate is highly unstable in the soil (Tisdale and Nelson, 1966). The formation of this compound is essentially the crossroad from which more varied transformation pathways of urea-N would emanate.

Volatilization. The formation of NH_3 during deamination of urea (Eq. [1]) is not the likely source of gaseous loss because of the readily available proton source in NH_2COOH. The main mechanism of NH_3 volatilization appears to be the following:

$$(NH_4)_2CO_3 \rightleftharpoons 2NH_4^+ + CO_3^{2-} \longrightarrow 2NH_3 + \underset{\text{(Carbonic acid)}}{H_2CO_3} \qquad [5]$$

The two moles of NH_3 are potentially volatilizeable, unless protons are available. Likely sources of protons are free acids and organic acids. The following reactions may prevent NH_3 from being lost through volatilization:

$$NH_3 + H^+ \longrightarrow NH_4^+ \qquad [5a]$$

$$RCOOH + NH_3 \longrightarrow RCOO^- + NH_4^+ \rightleftharpoons RCOO^-NH_4^+ \qquad [5b]$$

The formation of H_2CO_3 (Eq. [5]) depends upon the carbon dioxide (CO_2) equilibrium status between the soil and the atmosphere. Reactions involved in this process will not be covered in this paper. Excellent coverage of this subject was given by Hassett (1972).

Cation Exchange. Olson et al. (1971) gave the following reactions to show how NH_3 may be involved in cation exchange reactions:

$$]\text{-}H + NH_3 \longrightarrow]^- + NH_4^+ \rightleftharpoons]\text{-}NH_4 \qquad [6a]$$

$$]^{OH} + NH_3 \longrightarrow]^{O-} + NH_4^+ \rightleftharpoons]^{O-NH_4^+} \qquad [6b]$$

$$]\text{-}OH_2 + NH_3 \longrightarrow]\text{-}OH + NH_4^+ \quad [6c]$$

Reactions with bicarbonates (HCO_3^-) have two alternatives: the formation of H_2CO_3 (Eq. [7c]) or participation in cation exchange reactions. An exchange reaction with potassium (k) is shown below.

$$]\text{-}K + HCO_3^- + NH_4^+ \rightleftharpoons]\text{-}NH_4 + KHCO_3 \quad [6d]$$

pH Rise. During the first few days following urea addition to the soil, a rise in pH is usually observed. This rise is controlled by the reactions that are driven by the products of ureolysis. Although OH ions are not explicitly formed in Eqs. [5a] through [6c], these reactions are indirectly alkaline-producing since protons are utilized in the conversion of NH_3 to NH_4^+. Direct production of OH ions influencing pH rise is shown below.

$$CO_3^{2-} + 2H_2O \longrightarrow H_2CO_3 + 2OH \quad [7a]$$

$$CO_3^{2-} + H_2O \longrightarrow HCO_3^- + OH \quad [7b]$$

$$HCO_3^- + H_2O \longrightarrow H_2CO_3 + OH \quad [7c]$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH \quad [7d]$$

Only one mole of OH may be produced (Eq. [7b]) when the HCO_3^- ion is involved in reactions similar to Eq. [6d]. In Eq. [7d], leftward direction would seem to predominate because OH is more electronegative than NH_3 (Hart and Schuetz, 1972). However, if sinks for NH_4^+ are available at the moment of its formation (biological uptake or cation exchange reaction, for example), OH^- may be liberated to cause a pH rise. In general, high CEC, high free acid concentration, and abundant organic acids would tend to hold down volatile losses of NH_3 and buffer pH rise.

Other Consequences. The two moles of NH_4 that are produced for every mole of urea hydrolyzed may react with the concomitantly produced

CO_3. One or both moles may be nitrified, denitrified, leached, absorbed by roots, immobilized by microorganisms or the soil humus, or fixed by clays. Nitrification is the oxidation of NH_4 through microbial action (Eq. [8a]). On the other hand, denitrification is the evolution of N_2, N_2O, NO, NO_2 arising from the enzymatic reduction of NO_3 (Eq. [8b]). The following reactions were given by Olson et al. (1971):

$$NH_4 \xrightarrow{\text{Nitrosomonas}} NO_2 \xrightarrow{\text{Nitrobacter}} NO_3 \qquad [8a]$$

$$NO_3 \xrightarrow[\text{reduction}]{\text{enzymatic}} NO_2 \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2 \qquad [8b]$$

As mentioned earlier, high pH may inhibit the action of Nitrobacter more than that of Nitrosomonas such that NO_2 may accumulate and increase the potential of denitrification. The enzymatic reduction of NO_3 occurs under anaerobic conditions where NO_3 is used as a terminal proton acceptor in the decomposition of organic matter by facultative anaerobes, or when NO_3 is utilized as oxygen (O_2) source by autotrophic bacteria for the oxidation of inorganic compounds in the soil (Alexander, 1961; Olson et al., 1972).

Clay fixation of N may occur when, in the presence of K, the clay crystal lattice collapses and traps NH_4 (Olson et al., 1971). This process can be reversed or prevented in the presence of Ca and Mg.

MATERIALS AND METHODS

Soil Materials

Three soils (Leon fs, Bladen sl, and Plummer fs), typical of forested sites of the Southeastern Coastal Plain, were used in this study. Samples were taken from the A horizons (15 cm deep) in control plots in a series of CRIFF experiments (Pritchett and Smith, 1970).

The Leon series is a member of the sandy, siliceous, thermic family of Aeric Haplaquods. These sandy soils have thin, very dark gray A1 and light gray A2 horizons that total less than 76 cm thick, and dark humus B horizons. Samples were taken from a somewhat poorly drained site in Lake Butler, Florida. This site is one of those found to be highly responsive to N (especially if applied with P) fertilization (Pritchett and Smith, 1970).

The Bladen series is a member of the clayey, mixed, thermic family of Typic Ochraquults. These soils have loamy A horizons, gray, fine-textured, Bt horizons containing mottles of yellowish-brown, strong brown and shades of red, and a seasonally high water table. Samples were taken from a control plot of a field experiment which is located in a poorly drained site in Glynn County, Georgia. This site was not as N responsive as the Leon site, but this soil was selected because of its high clay content (Table 1) which influences urea-N mobility.

The Plummer series is a Grossarenic Ochraquult[1/] member of a loamy siliceous, thermic family. Plummer soils typically have thin, gray to

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1/ This is a provisional subgroup.

Table 1. Selected chemical and physical properties of three forest soils of the Southeastern Coastal Plain

Soil type	pH[a]	N[b]	OM[c]	Total sand[d]	Silt[d]	Clay[d]	CEC[d]
				%			meq/100g
Leon	4.3	0.026	0.92	88.0	10.0	2.0	7.7
Bladen	4.2	0.081	2.75	52.0	30.0	18.0	12.6
Plummer	3.5	0.385	20.00	64.0	25.0	11.0	21.5
Plummer + D[e]	3.5	0.710	25.00	-	-	-	-

[a]Soil pH using 1:1 soil-water suspension. Unless otherwise specified, all soil pH data reported in these studies are determined in the same manner.

[b]Total N by salicylic acid modification of the macro-Kjeldahl method.

[c]Organic matter content by potassium dichromate oxidation method.

[d]From the CRIFF Uniform Fertilizer Experiments Installation Report.

[e]Samples consisting of loose debris that did not pass through the 2-mm sieve.

black A1 horizons underlain with thick, gray to white sandy A2 horizons; these horizons overlie a strongly gleyed, loamy argillic horizon. Samples were taken from a control plot of a field experiment located in a poorly drained site near palatka, Florida. The CRIFF Progress Report (Unpublished data, UF, Gainesville, FL, 1971) indicated that 22 kg N/ha elicited a negative height growth response while 90 kg N/ha effected greater height growth than the unfertilized plots. This soil was selected for this study because of its high organic matter content (Table 1) which has some influence on urea-N transformations.

With these soils comparisons of the movement and transformation of urea-N in soils with low organic matter and clay contents (Leon fs), high clay content (Bladen), and high organic matter content (Plummer fsl) were possible. Chemical and physical properties of the soils are given in Table 1.

Experiment 1. Incubation

Fifty-gram samples of oven-dry Leon soil were each weighed into screw-cap glass jars. Three levels of urea-N (0, 118, and 236 ppm) were added and thoroughly mixed with the soil. Four soil moisture regimes defined by a soil moisture retention curve (Fig. 2) were maintained. Thus, on an oven-dry weight basis, 25.0, 5.4, 2.5, and 1.8 % of water was needed to effect soil moisture regimes having soil matric suction of 0, 100, 345, and 1000 cm of water, respectively. Each treatment was replicated twice on each soil moisture regime (see Experimental design, Table 2A). The caps of the glass jars were replaced with perforated aluminum foil which

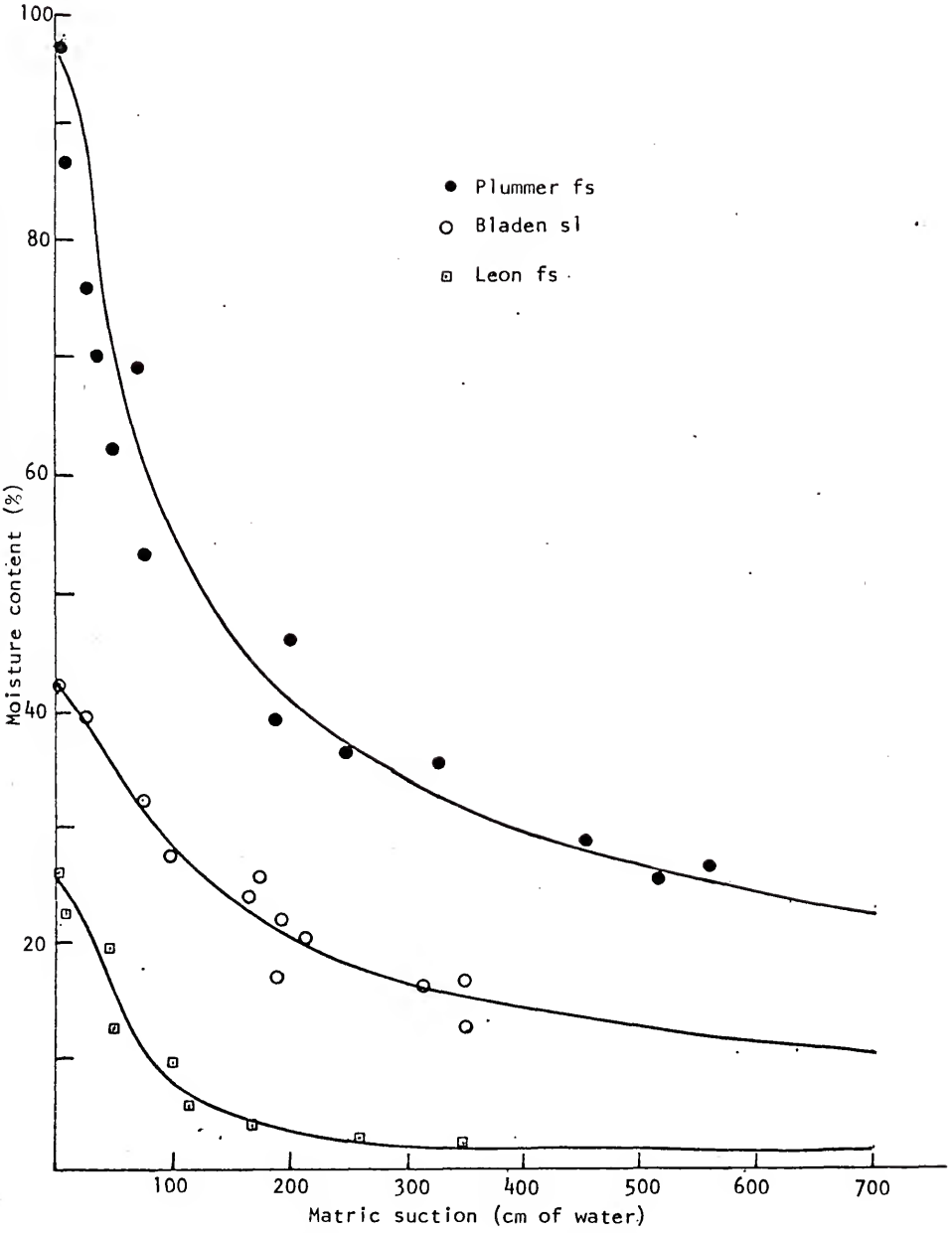


Fig. 2. Moisture retention curves of three forest soils of the Southeastern Coastal Plain.

Table 2. Experimental designs

A. Experiment 1. Incubation

Urea-N treatment	Soil moisture regimes (cm of water)			
	0	100	345	1000
	N added, ppm			
1	0	0	0	0
2	118	118	118	118
3	236	236	236	236

Note: Number of replications = 2; number of samplings = 5.

B. Experiment 2A. Lysimeter pots with two-year-old slash pine

Treatment symbol[a]	Soil moisture regimes (cm of water)	
	170	500
	N added, kg/ha	
0	0	0
U1	224	224
S1	224	224
U2	448	448
S2	448	448

[a]Treatment symbols: 0 = no N added; U1 = N added as urea; S1 = N added as ammonium sulfate; U2 = 2 x U1; S2 = 2 x S1.

Note: Number of replications = 4.

C. Experiment 2B. Lysimeter pots with one-year-old slash pine

Treatment symbols[a]	Shaded side[b]	Exposed side
	N added, kg/ha	
0	0	0
U1	224	224
S1	224	224
U2	448	448
S2	448	448

[a]See footnote a, Table 2B.

[b]Shaded side did not receive direct sunlight while the exposed side received direct sunlight during most of the day.

Note: Number of replications = 2.

Table 2. continued.

D. Experiment 3. Greenhouse soil columns

Soil type	Soil moisture regimes (cm of water)			
	170		500	
	kg N/ha			
Leon	0	448	0	448
Bladen	0	448	0	448
Plummer	0	448	0	448
Plummer + D[a]	0	448	0	448

[a]Soil columns overlain with Plummer debris that did not pass through the 2-mm sieve.

Note: Number of replications = 2.

E. Experiment 4. Laboratory soil columns

Soil type	Days after fertilization			
	2		5	
	PMA[a] added, ppm			
Leon	0	50	0	50
Bladen	0	50	0	50
Plummer	0	50	0	50
Plummer + D[b]	0	50	0	50

[a]PMA = phenylmercuric acetate.

[b]See footnote a, Table 2D.

Note: Urea-N was added at a uniform rate of 100 ppm.
Number of replications = 2.

was fitted to each jar with a rubber band. The samples were incubated at 28 C. Moisture conditions were maintained for each regime by watering to the original moisture levels twice a week through weight adjustment. Subsamples were collected 2 days, 1 week, 2 weeks, 4 weeks, and 6 weeks after fertilization and extracted for pH determination, and urea-N, NH_4-N, and NO_3-N analysis. At the end of 1 week, soil extractions from samples under soil moisture regime of 100 cm of water were plated so that ureolytic mircoorganisms could be quantified and some indentified (Skerman, 1959).

Experiment 2A. Lysimeter Pots with Two-year-old Slash Pine

In May, 1972, two-year-old slash pine seedlings were planted in 4-gallon glazed ceramic lysimeter pots (Fig. 3A) with Leon soil. Since the pots were flat-bottomed, a soil moisture potential profile was established to determine the possibility of waterlogging at the pot bottoms (22 cm below the surface) as this would affect the overall experimental design. Tensiometers were installed at two depths (1cm and 21 cm below the soil surface) in the pots with and without seedlings. Results indicated that no such waterlogging occurred (Fig. 4).

In April, 1973, all pots were uniformly fertilized with P as concentrated superphosphate (CSP), K as potassium chloride (KCl), and fritted trace elements (FTE 503) at rates equivalent to 112, 90, and 112 kg/ha, respectively. Nitrogen from two sources, $[(NH_2)_2CO$ and $(NH_4)_2SO_4]$, was added at three levels: 224, and 448 kg/ha. The N treatments, replicated four times, were randomized over every ten pots (Table 2B). The fertilizers were spread on the soil surface and covered with an additional 2-cm layers of the same soil.

Fig. 3A. Two-year-old slash pine grown in four-gallon glazed ceramic lysimeter pots filled with Leon soil.

Fig. 3B. One-year-old slash pine grown in round-bottomed, three-gallon glazed ceramic lysimeter pot filled with Leon soil.

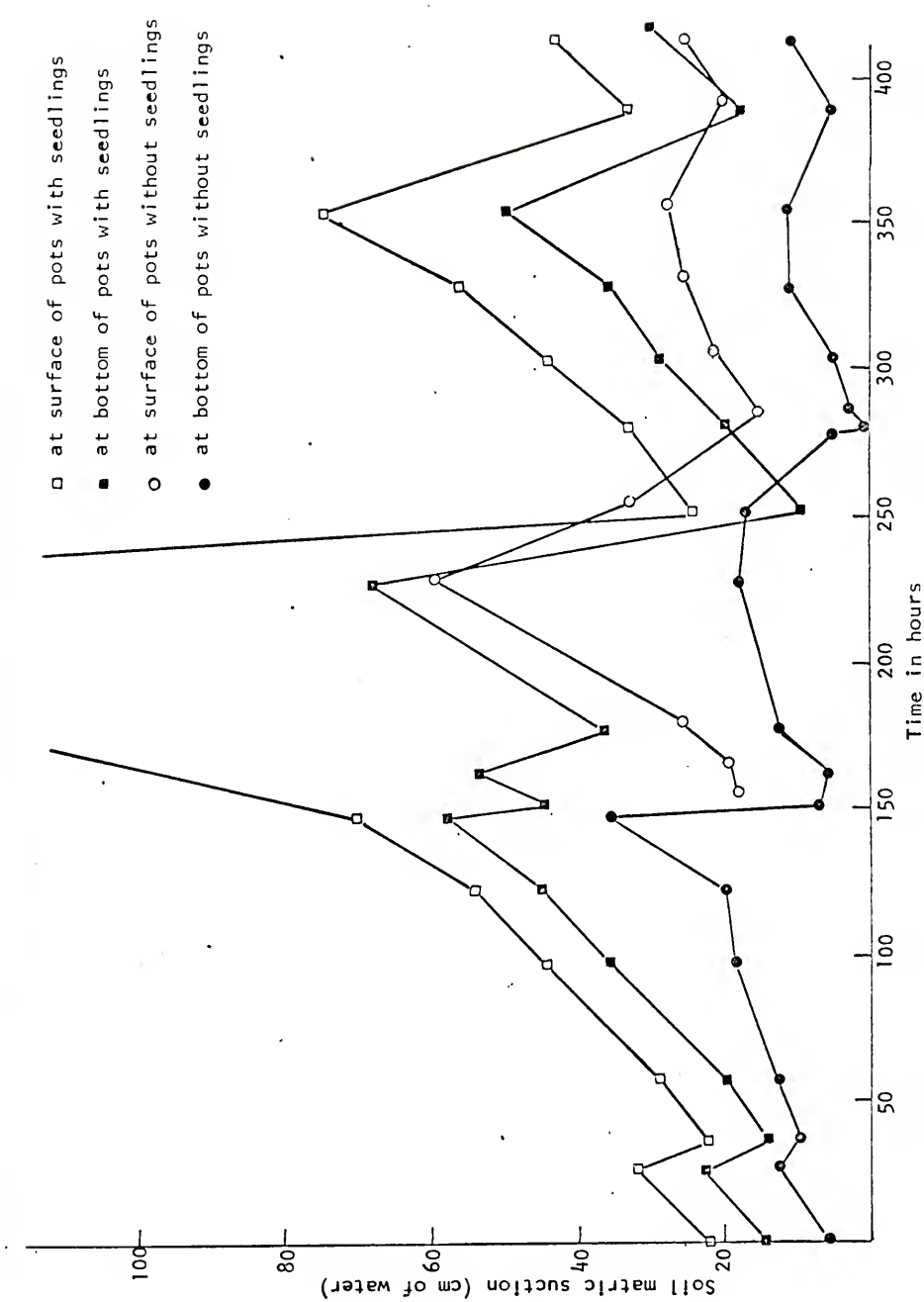


Fig. 4. Variations in soil matric suction at the surface and bottom of pots with and without seedlings.

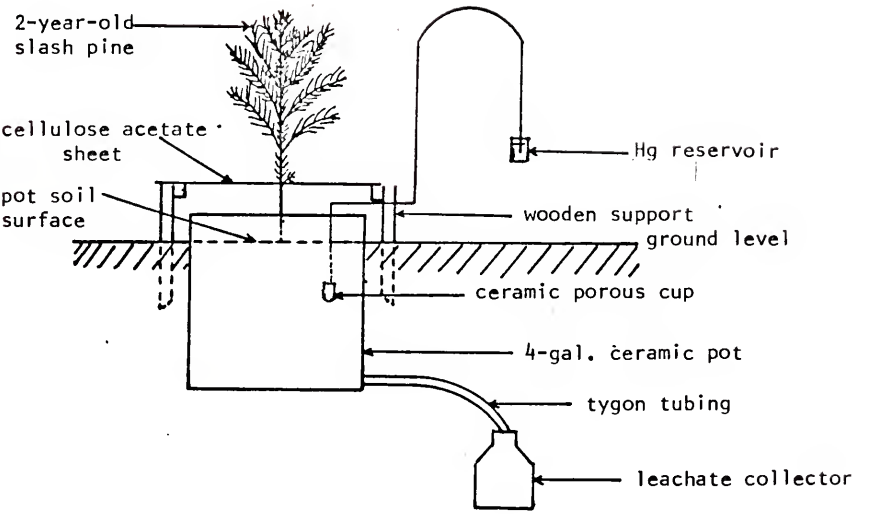
Since the lysimeter pots were in the open, moisture input was regulated by covering the pots, but not the seedlings, with cellulose acetate sheets (Fig. 5A). Two soil moisture regimes, 170 and 500 cm of water, were maintained as indicated by tensiometers which were installed at 10 cm below the soil surface. Each time the soil moisture potential limits were approached, distilled water was added at amounts such that 400 to 500 ml of leachate was produced. The leachates were stored in plastic beakers or bottles and refrigerated. Two months after fertilization, the cellulose acetate sheets were removed. When no rainfall occurred for a sustained period, the soil moisture regimes were maintained by adding enough distilled water to bring the soil matric suction at the pot bottom close to 0 cm of water (tensiometer readings of 10 to 15 cm of water indicated such condition). Samples of leachates produced due to excessive rainfall were stored in plastic bottles and refrigerated. Height and diameter were measured at the time of fertilization and once a month thereafter.

Experiment 2B. Lysimeter Pots with One-year-old Slash Pine

In June, 1972, slash pine seeds were sown in lysimeter pots filled with Leon soil. When the seedlings were one year old, they were transplanted to 3-gallon, round-bottomed, glazed ceramic lysimeter pots attached to the sides of the lysimeter pit (Figs. 3B and 5B). One bench did not receive direct sunlight (designated as Shaded Side) while the other bench received direct sunlight during most of the day (designated as Exposed Side).

In July, 1973, (two weeks after transplanting), all pots uniformly received the same rates and sources of P, K, and micronutrients, the same rates and sources of N, and the same randomization scheme as in

A. Experiment 2A



B. Experiment 2B

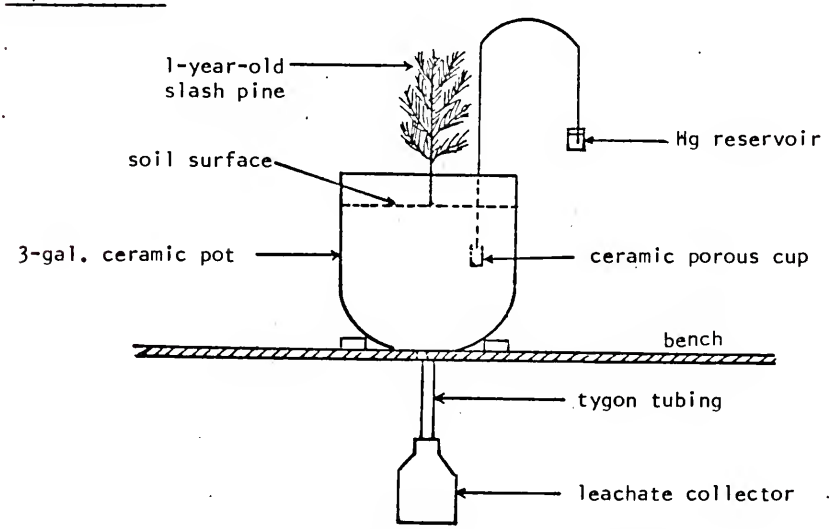


Fig. 5. Schematic diagram of the lysimeter systems employed in Experiments 2A and 2B.

Experiment 2A. The N treatments were replicated two times over each bench (Table 2C). Moisture input due to rain was not controlled. When no rainfall occurred for a sustained period, distilled water was added to prevent soil moisture potential from exceeding 170 cm of water. Leachates were sampled, stored in plastic bottles and refrigerated. Height and diameter were measured at the time of fertilization and once a month thereafter.

In January, 1974, after measuring their final height and diameter, the seedlings in both experiments were harvested. Foliage, stems, and roots of each seedlings were separated and dried in an air-circulated oven at 70 C for 3 to 4 days. After obtaining the dry weights, the samples were ground in a Wiley mill to pass a 20 mesh screen. The soil in the pots was sampled for analysis of pH and residual N, P, K, Ca, and Mg.

Experiment 3. Greenhouse Soil Columns

Plexiglass tubes (11.75 cm in inside diameter) were cut into 38-cm sections. One end of each section was sealed with a cut-out plexiglass panel through which a rubber stopper fitted with a glass tubing was inserted to provide a leaching outlet. The plexiglass columns were placed on two racks and divided into four sets. The first set (L) was filled with Leon fs, the second set (B) with Bladen sl, the third set (P) with Plummer fs, and the fourth set (PD) with Plummer fs overlain with 4-cm layers of loose organic debris that did not pass the 2-mm sieve (Table 1). Tensiometers were installed through the side of each column at 10 cm below the soil surface. Slash pine seeds were sown in a seedbox and one seedling was transplanted to each soil column. When the seedlings were three months old, the columns were uniformly

fertilized with P, K, and micronutrients at the same rates and sources as in Experiments 2A and 2B. Nitrogen as urea was added at rates equivalent to 0 and 448 kg/ha. Two soil moisture regimes were maintained. In one soil moisture regime (W1), distilled water was added two days after fertilization at amounts sufficient to produce about 150 ml of leachate which was stored in plastic beakers and refrigerated. Each time the soil moisture potentials reached 170 cm of water, distilled water was added to bring the soil matric suction at the bottom of the soil column close to 0 cm of water (tensiometer readings of 30 to 35 cm of water indicated such condition) when no leachate was desired. Sufficient amounts of distilled water were instantaneously added to produce about 150 ml of leachate whenever desired. In W1, there were three leachings made. In the other soil moisture regime (W2), distilled water was added one week after fertilization and once a week thereafter or whenever the soil moisture potentials reached 500 cm of soil water tension. Only one leaching was made in W2. The soil types were randomized with two replications for each N level and soil moisture regime (see experimental design, Table 2D).

For trapping the NH_3 volatilized from the urea applied, a system of acidified NH_3 sorbers similar to the one employed by Nommik (1973a) was used (Fig. 6). This consisted of two foam rubber discs fitted tightly inside a polyvinyl chloride (PVC) pipe (12.7 cm in length and 4.3 cm in inside diameter). Before using, the discs were leached alternately with 1 M H_3PO_4 and 1 M KOH, and finally with deionized water. The discs were then soaked in a solution containing 50 ml of 85 % H_3PO_4 and 40 ml of glycerol per liter. The excess solution in each sorber was removed by squeezing. To check NH_3 contamination of the

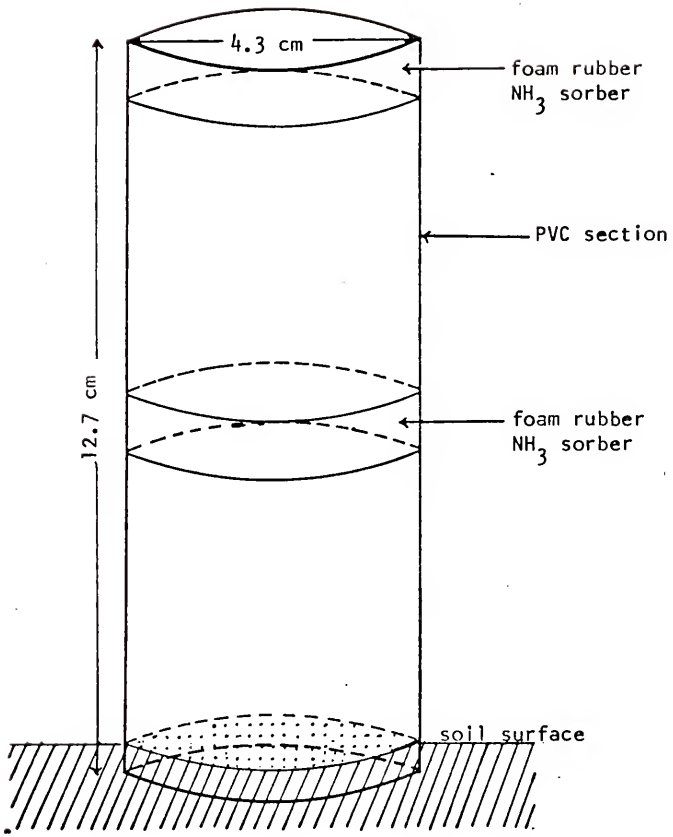


Fig. 6. Device for trapping ammonia volatilized from urea applied to the soil columns in the greenhouse.

system, four sorbers were placed on unfertilized soil columns.

The sorbers were replaced 1, 3, 5, 9, 14, and 21 days after fertilization. The discs removed from the used sorbers were successively leached with five 10-ml portions of 1 N KCl containing 6 ppm of phenylmercuric acetate (PMA). The leachates were stored in plastic beakers and refrigerated until analyzed.

The soil columns were sampled at three depths with a soil auger. The soil samples were placed in polyethylene bags and stored under refrigeration.

Experiment 4. Laboratory Soil Columns

Four sets of PVC sections (12.7 cm in length and 4.3 cm in inside diameter) were prepared. The first set (four sections per set) was filled with Leon fs, the second with Bladen sl, the third set with Plummer fs, and the fourth with loose debris of the Plummer fs that did not pass the 2-mm sieve. The amount of soil placed in each section was such that a 10-cm soil column was attained. Each set was divided into two subsets. To one subset, PMA was added at the rate of 50 ppm and throughly mixed with the soil. Experimental design is shown in Table 2E.

Each soil column was placed on a glass funnel provided with a filter paper (Watman No. 42). The soil columns were then supersaturated with deionized water and allowed to drain. When drainage stopped, a solution of urea-N was added to each soil column at a uniform rate of 100 ppm. Foam rubber discs (prepared in the same manner as in Experiment 3) were fitted tightly at the top of each column. Two days after fertilization, the foam rubber discs were removed from half of the soil columns and leached with 1 N KCl containing 6 ppm of PMA.

The leachates were stored in plastic beakers and refrigerated. Each soil column of this set was leached with deionized water in sufficient amounts to produce about 120 ml of leachates. When drainage stopped, the soil columns were sampled into 5-cm sections, stored in polyethylene bags, and refrigerated. The same procedure was repeated for the remaining set of soil columns 5 days after fertilization.

Analysis of Leachates

For Experiments 2A and 2B, leachate pH was measured using a glass electrode and potentiometer. Analysis of urea-N was done by a colorimetric method (Douglas and Bremner, 1971). Determination of NH_4-N was made by steam distillation, NO_3-N by Devarda's alloy treatment followed by steam distillation, except for the months of June and July when high rainfall frequencies and intensities (Table 3) resulted in large amounts of leachate. Since determination of NH_4-N and NO_3-N by the above methods is relatively slow, NH_4-N was analyzed using the ammonia selective electrode (ASE) and NO_3-N was determined using the nitrate specific ion electrode (NSIE) during these months. Compared to the steam distillation method of NH_4-N determination, accuracy of the ASE is very high (Banwart et al., 1972; Thomas and Booth, 1973). The NSIE allows significant interference of chloride (Cl^-) when the concentration of the latter exceeds ten times that of NO_3. Table 4 appears to indicate that such interference did not occur. To verify the accuracy of ASE method, some electrode measurements were calibrated against steam distillation (SD) measurements. For NH_4-N concentrations greater than 1.0 ppm, the ASE method was adequately comparable with the SD method, as indicated by the high correlation coefficient (Fig. 7).

Subsamples of the leachates were sent to the Soil Science

Table 3. Rainfall over the experimental site during the period April to December, 1973

Month	Date	Rainfall (cm)	Month	Date	Rainfall (cm)
April	11 - 30	none	July	30	2.0
				31	0.5
May	1 - 30	0.0			
June	8	1.5	August	3	0.2
	12	3.8		6	0.4
	13	4.3		7	0.5
	15	1.8		16	3.6
	18	1.8		19	0.8
	21	6.2		21	2.3
	22	5.8			
	23	0.3	September	1 - 3	6.4
	27	1.0		4	0.5
				15	2.0
July	7	2.3		25	1.3
	8	2.3		28	0.8
	9	4.6			
	12	1.0	October	6	0.6
	15	2.0		21	0.8
	17	0.5		31	1.9
	18	0.5			
	22	1.5	November	29	0.5
	27	0.2			
	28	0.9	December	8	4.6
	29	1.9		16	7.6
				20	2.3

Table 4. Leachate concentrations of nitrate and chloride

Sample #	NO_3 SD[a]	NO_3 SI[b]	Cl SI	Sample #	NO_3 SD	NO_3 SI	Cl SI
	ppm				ppm		
1	5	10	44	21	403	450	7
2	34	36	115	22	465	330	11
3	0	2	32	23	83	69	8
4	0	7	57	24	466	400	10
5	63	120	2	25	86	135	4
6	74	125	3	26	236	235	4
7	156	165	10	27	16	22	2
8	82	60	10	28	270	245	2
9	182	185	10	29	131	120	3
10	221	180	27	30	18	26	0
11	301	330	10	31	531	560	17
12	66	49	7	32	0	8	3
13	260	280	38	33	80	68	4
14	168	105	15	34	34	36	115
15	363	260	5	35	6	12	20
16	18	22	15	36	9	16	18
17	27	31	46	37	0	1	20
18	2	8	16	38	13	18	24
19	22	27	29	39	0	2	20
20	0	1	17	40	5	10	12

[a]Determined by Devarda's alloy treatment followed by steam distillation.

[b]Determined by specific ion electrode method.

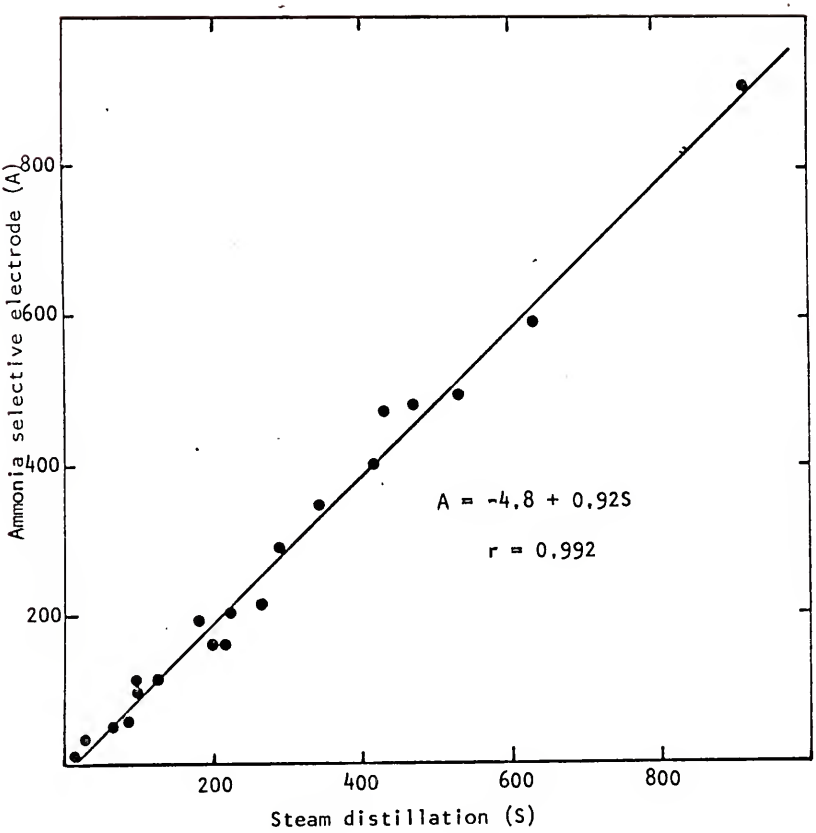


Fig. 7. The relationship between ammonium-N values (ppm) determined by steam distillation and ammonia selective electrode methods.

Department Analytical Research Laboratory where P was determined by the ascorbic acid method (Watanabe and Olsen, 1965), K by flame emission spectrophotometer, Ca and Mg by atomic absorption spectrophotometer, and soluble salts by electrical conductivity method.

Leachates collected in Experiments 3 and 4 were analyzed for pH, urea-N by colorimetric method (Douglas and Bremner, 1971) NH_4-N by steam distillation, and NO_3-N by Devarda's alloy treatment followed by steam distillation.

The leachings from the NH_3 sorbers were analyzed for NH_3-N by making 10-ml aliquots alkaline with 5 ml of 10 N NaOH immediately prior to steam distillation. The amount of N detected in this system was considered NH_3-N volatilization loss.

Soil Extraction and Analysis

Soil samples in Experiments 2A and 2B were dried and sieved through a 2-mm mesh. Total N was determined by the salicylic modification of the macro-Kjeldahl method. For pH and KCl-extractable N (NH_4-N and NO_3-N) determinations, the following were perfromed: Ten-gram air-dry soil samples were weighed into 100-ml plastic beakers. After adding 10 ml of deionized water, the soil suspension was shaken for 15 minutes in a mechanical shaker. After the pH determination, 20 ml of extracting solution (2 N KCl containing 6 ppm of PMA) was added and the suspension was shaken in a mechanical shaker for 45 minutes. The soil suspension was then poured into a leaching tube provided with a filter paper (Watman No. 42) and followed by two 15-ml portions of the extracting solution. The filtrates were transferred to plastic beakers marked at 60 ml, made to volume with the extracting solution, and stored in the refrigerator. Soil subsamples were analyzed for residual P, K, Ca and

Mg after extracting the soil with 1 N NH_4OAc (pH 4.8). Phosphorus was determined by ammonium molybdate-stannous chloride colorimetric method (Jackson, 1958), K, Ca, and Mg by the methods previously described.

Soil samples in Experiments 1, 3, and 4 were analyzed without being dried. Moisture content of each sample was determined on an oven-dry weight basis. In Experiment 3, total N analysis and soil extraction for pH, urea-N, NH_4-N, and NO_3-N determinations were done as above. Since the soil samples were not dried, addition of deionized water for pH determination was done such that the total water content would effect a 1:1 ratio by weight with the soil. Soil extracts in Experiment 3 were analyzed for KCl-extractable organic N by micro-Kjeldahl digestion method (Bremner, 1965). In the characterization of the different N fractions in the soil, the difference between total N as determined by macro-Kjeldahl method and the amount of KCl-extractable N was considered non-extractable N. The difference between total KCl-extractable N as determined by micro-Kjeldahl digestion followed by steam distillation and the amount of N detected as NH_4-N and NO_3-N was considerd KCl-extractable organic N. Conceivably, the KCl-extractable organic N may include some of the added urea-N that may have remained unhydrolyzed.

Tissue Analysis

Total N was analyzed from 1.0 g of the ground tissue by the salicylic modification of the macro-Kjeldahl method. For the analysis of P, K, Ca, and Mg, 2-gram ground tissue samples were dry-ashed at 500 C in a muffle furnace and the ash was dissolved in 50 ml 0.1 N HCl. Phosphorus was determined by the ascorbic acid method, K, Ca, and Mg by the methods previously described.

RESULTS

Experiment 1. Incubation

Platings of the extracts from soil incubated for 1 week gave quantitative results which indicated a positive response of ureolytic microorganisms to urea treatment (Table 5). The stimulative effect of urea was not limited to ureolytic microorganisms; the total microbial population increased more than four-fold and seven-fold when 118 ppm and 236 ppm urea-N, respectively, were added. While 118 ppm urea-N effected a population increase of ureolytic microorganism at the same rate (four-fold) as that of the total microbial population, 236 ppm urea-N caused the population of ureolytic microorganism to increase about ten-fold more than the total population.

The urease-agar used in the platings had an initial pH of 6.9 and a yellowish color. Presence of ureolytic microorganisms was indicated by a halo of changing color (from yellow to purple) of the culture medium around the developing colony. This color change resulted from a rise in pH as NH_3-N was produced during or after ureolysis. Fungal ureolytic colonies germinated earlier and grew much faster than the bacterial colonies. Subcultures taken from the ureolytic colonies revealed a rather wide spectrum of microbial species (See note, Table 5) that were apparently capable of producing the enyzme urease.

The effects of soil moisture regimes, urea-N treatment, and length of incubation period on the disappearance of unhydrolyzed urea-N, formation of NH_4-N and NO_3-N, and soil pH are shown in Table 6.

Table 5. The effects of urea ization 00 cm of water tension on ulation olytic microorganism in the after or of incubation

N Added (ppm)[a]	Total MO[b]/g soil	UMO[c]/g soil	% UMO
0	3.7×10^6	0.1×10^6	3.0
118	13.5×10^6	0.4×10^6	3.0
236	20.0×10^6	1.0×10^6	5.0

[a]Nitrogen added as urea.

[b]MO = microorganism.

[c]UMO = ureolytic microorganism.

Note: The microorganisms identified from the isolates were:

Fungi: Pyronelaea, Penicillium, Fusarium, Trichoderma, Sartoria, Aspergillus, and Sporotrichum;

Bacteria: gram positive cocci and rods and one negative rod;

Yeast: gram positive.

Table 6. Statistical analysis of parameters measured in Experiment 1: Incubation for forty-two days of a Leon soil treated with three levels of urea-N under four soil moisture regimes

A. Significance of the effects of soil moisture regimes, rates of urea-N, and incubation period on extractable urea-N, NH_4-N, and NO_3-N and soil pH

Parameters	Soil moisture regimes (W)[a]	Urea-N rates (T)[b]	Incubation period (P)[c]	W x T
Urea-N	**	**	**	*
NH_4-N	**	**	**	*
NO_3-N	**	**	**	NS
Soil pH	**	**	**	**

B. The effects of soil moisture regimes and rates of urea-N on extractable urea-N and NH_4-N and soil pH

	Soil moisture regimes (cm of water)											
	0			100			345			1000		
Parameters	0[d]	118	236	0	118	236	0	118	236	0	118	236
Urea-N (%)[e]	0.0b[f]	10.4a	15.9a	0.0a	9.1a	8.3a	0.0b	15.1a	16.8a	0.0c	20.0b	29.7a
NH_4-N (%)	3.4b	14.3a	15.9a	3.6b	17.4a	22.4a	3.5b	14.0a	17.4a	3.1a	5.1a	8.5a
Soil pH	4.3b	5.9a	6.2a	4.5c	6.2b	7.0a	4.4c	5.8b	6.7a	4.6b	5.1ab	5.7a

Table 6. continued.

C. The effects of soil moisture regimes on extractable urea-N, NH_4-N, and NO_3-N and soil pH

Parameters	Soil moisture regimes (cm of water) 0	100	345	1000
Urea-N (%)	8.8bc	5.8c	10.7b	16.6a
NH_4-N (%)	11.2a	14.5a	11.6a	5.6b
NO_3-N (%)	1.6bc	2.2a	1.3c	1.3c
Soil pH	5.5bc	5.9a	5.6ab	5.2c

D. The effects of urea-N rates on extractable urea-N, NH_4-N, and NO_3-N and soil pH

Parameters	Urea-N added (ppm) 0	118	236
Urea-N (%)	0.0c	13.6b	17.9a
NH_4-N (%)	3.4c	12.7b	16.1a
NO_3-N (%)	2.3a	1.8b	0.7c
Soil pH	4.4c	5.8b	6.4a

Table 6. continued.

E. The effects of varying lengths of incubation period on extractable urea-N, NH_4-N, and NO_3-N and soil pH

Parameters	Incubation period (days) 2	7	14	28	42
Urea-N (%)	23.5a	14.6b	5.6c	4.7c	3.7c
NH_4-N (%)	2.6e	7.7d	17.3a	11.9c	14.1bc
NO_3-N (%)	1.6bc	1.7ab	1.2c	2.1a	1.3bc
Soil pH	4.1c	5.0b	6.2a	6.3a	6.1a

[a]Soil moisture regimes (cm of water): 0, 100, 345, and 1000.

[b]Urea-N levels (ppm): 0, 118, and 236.

[c]Incubation period in days.

[d]See footnote b above.

[e]Extractable urea-N, NH_4-N, and NO_3-N are expressed as percent of the total initial N.

[f]Differences in letters across each parameter indicate significant differences (at .05 level) between means as indicated by Duncan Multiple Range test.

Note: For measures of statistical precision, see Table 18.
* = significant at .05 level; ** = significant at .01 level;
NS = non-significant.

by urea-N treatment within each soil moisture regime is shown in Table 6B. Under 0 cm of soil water tension, urea-N that remained unhydrolyzed amounted to 10.4 and 15.9 % of the total soil N with urea-N treatments of 118 and 236 ppm, respectively. When the soil matric suction was maintained close to 100 cm water, the percentage of urea-N that remained unhydrolyzed was no longer significant. Ammonification under this soil moisture regime was increased by urea-N addition, although the effects of the two levels of urea-N (118 and 236 ppm) were not different. Levels of urea-N distinctively influenced changes in soil pH, with pH rising from 4.5 where no urea-N was added to 7.0 where 236 ppm were applied.

Maintaining soil moisture conditions close to 345 cm of soil water tension elicited effects on ureolysis and ammonification that were nearly identical with those observed under 0 cm of soil water tension. The differences in soil pH with respect to N levels followed the following order: 0 < 118 < 236 ppm urea-N.

When soil matric suction was maintained close to 1000 cm of water, the amount of unhydrolyzed urea-N recovered from samples receiving 236 ppm urea-N was significantly greater than from those receiving 118 ppm urea-N. Urea-N treatment did not increase ammonification under this soil moisture regime. Addition of 236 ppm urea-N caused soil pH to rise slightly more than either 0 or 118 ppm urea-N (Table 6B).

The effects of soil moisture regimes on ureolysis, ammonification, nitrification, and soil pH change are shown in Table 6C. Maintaining soil matric suction close to 100 cm of water seemed to provide the best environment for rapid ureolysis. Under this soil moisture regime, the overall average amount of urea-N that remained unhydrolyzed was least.

Ureolysis was affected by soil moisture levels as follows: 100 $\geq$ 0 $\geq$ 345 $\geq$ 1000 cm of soil water tension. Maintaining soil matric suction as high as 1000 cm of water, however, reduced ammonification. Nitrification occurred at a rather low level of production, especially under 0, 345, and 1000 cm of soil water tension. It was only under 100 cm of soil water tension that nitrification was significantly higher. Overall changes in soil pH were slightly affected by soil moisture regimes in the following order: 100 $\geq$ 345 $\geq$ 0 $\geq$ 1000 cm of water.

The overall effects of urea-N treatments on ureolysis and ammonification were in the following order: 236 > 118 > 0 ppm urea-N Table 6C). Addition of 118 ppm urea-N appear to slightly increase nitrification while 236 ppm urea-N tended to reduce it. For instance, the percentages shown in Table 6D represent NO_3-N production of 0.30, 0.34, and 0.17 mg resulting from urea-N treatments of 0, 118, and 236 ppm, respectively. Changes in soil pH resulting from urea-N treatments occurred in the following order: 236 > 118 > 0 ppm urea-N.

The amount of urea-N that remained unhydrolyzed was higher after 2 days than either of the subsequent incubation periods (Table 6D). Residual urea decreased after 7 days of incubation and even further after 14 days of incubation. The amount of urea-N recovered after the longer incubation periods (28 and 42 days) was negligible. Ammonification was minimum (NH_4-N = 2.6 % of total N) during 2 days of incubation, but increased to 7.7 % of total N after 7 days and reached a maximum value of 17.3 % of the total N after 14 days. Ammonification decreased during the period 14 to 28 days and remained unchanged 28 to 42 days after fertilization. The amounts of NH_4-N produced during the last two incubation periods were greater than those produced during the first week of incubation. Nitrification did not seem to fluctuate as

widely as ammonification. A maximum production of NO_3-N (2.1 %), which was higher than those detected at the end of 2, 14, and 42 days, was attained by incubating the soil for 28 days. Soil pH changed from 4.3 at the beginning of the incubation period to 4.1, 5.0, and 6.2 after 2, 7, and 14 days, respectively, but remained fairly constant thereafter.

Under 100 cm of soil water tension, complete disappearance of unhydrolyzed urea-N occurred in 7 and 14 days after adding 118 and 236 ppm urea-N, respectively (Fig. 8B). Ureolytic activity was reduced when soil matric suction was maintained near 345 cm of water (Fig. 8C) and least efficient ureolysis occurred when the soil was kept under higher soil matric suction (Fig. 8D). For a sandy soil such as Leon, 1000 cm of soil water tension probably approaches the wilting point. Under 0 cm of soil water tension, there seemed to be a quiescent period (2 to 7 days) during which the ureolytic microorganisms apparently slowed down in their activity (Fig. 8A). After 7 days of incubation, the ureolytic rate increased again, which finally resulted in complete disappearance of unhydrolyzed urea-N during 28 to 42 days of incubation.

The ammonification process also showed characteristic patterns. Under 0 and 100 cm of soil water tension (Fig. 8A and 8B) peak production of NH_4 coincided with the complete hydrolysis of urea-N. However, after its maximum production, NH_4-N decreased and apparently reached minimum levels at about 28 days after fertilization. The rate of decrease was faster under 0 than 100 cm of soil water tension. During the period 28 to 42 days of incubation, ammonification increased again with 0 cm of soil water tension favoring a slightly higher rate of increase than 100 cm of soil water tension. Although the average ammonification process under

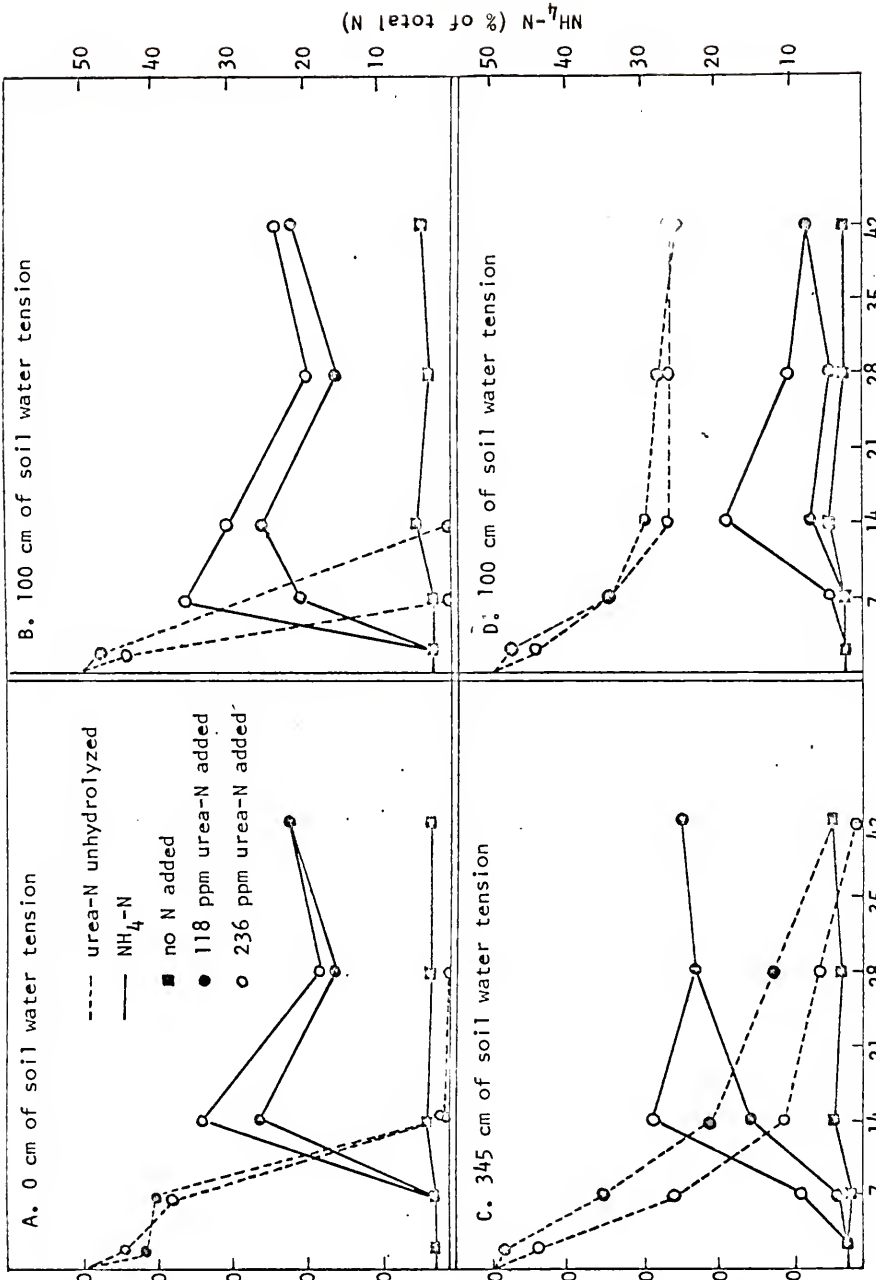

A. 0 cm of soil water tension
B. 100 cm of soil water tension
C. 345 cm of soil water tension
D. 100 cm of soil water tension
urea-N unhydrolyzed
NH_4-N
no N added
118 ppm urea-N added
236 ppm urea-N added
Urea-N (% of added N)
NH_4-N (% of total N)
Incubation period (days)

Fig. 8. The effects of soil moisture regimes, urea-N levels, and incubation period on ureolysis and ammonification.

345 cm of soil water tension vary from those that occurred under 0 and 100 cm of soil water tension (Table 6C), the pattern was different (Fig. 8C). Under this soil matric suction (345 cm of water), 118 ppm urea-N effected a steady build-up of NH_4-N during the whole experimental period. On the other hand, NH_4-N production resulting from the addition of 236 ppm urea-N showed a decline after its peak production at about the 14th day of incubation. Under 1000 cm of soil water tension, about 19 % of the total initial soil N was in the NH_4-N form 14 days after the addition of 236 ppm urea-N. However, after peak production at the 14th day, NH_4-N steadily declined until the end of the experimental period. A slight build-up of NH_4-N resulted from the addition of 118 ppm urea-N under the same soil moisture condition.

Nitrification occurred at a much lower level than ammonification (Fig. 9). Maximum nitrification generally occurred under 100 cm of soil water tension (Table 6C). The highest NO_3-N concentration (19.2 ppm, soil basis) was detected 28 days after fertilization with 118 ppm urea-N under 100 cm of soil water tension (Fig. 9B). Nitrification resulting from the addition of 236 ppm urea-N under 0 and 100 cm of soil water tension fluctuated with the length of incubation period. On the other hand, nitrification under 345 and 1000 cm of soil water tension appeared to steadily decline with increasing length of incubation period (Fig. 9C and D). Nitrate-N production in the unfertilized samples fluctuated with the different incubation periods under 100 and 345, remained essentially steady under 1000, and steadily declined under 0 cm of soil water tension.

Incubating the unfertilized samples for 2 days under 0 cm of soil water tension caused soil pH to drop from 4.3 to 3.6 (Fig. 10A). With

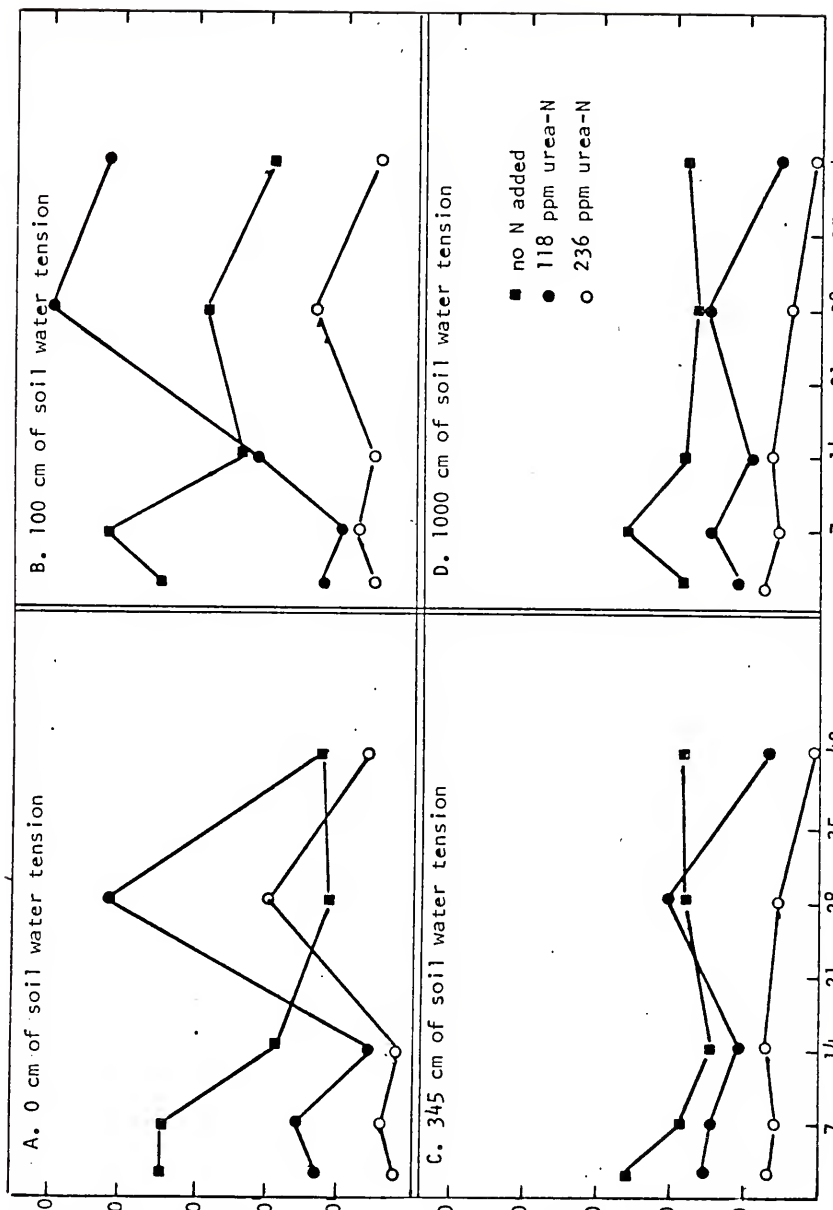


Fig. 9. The effects of soil moisture regimes, urea-N levels, and incubation period on nitrification.

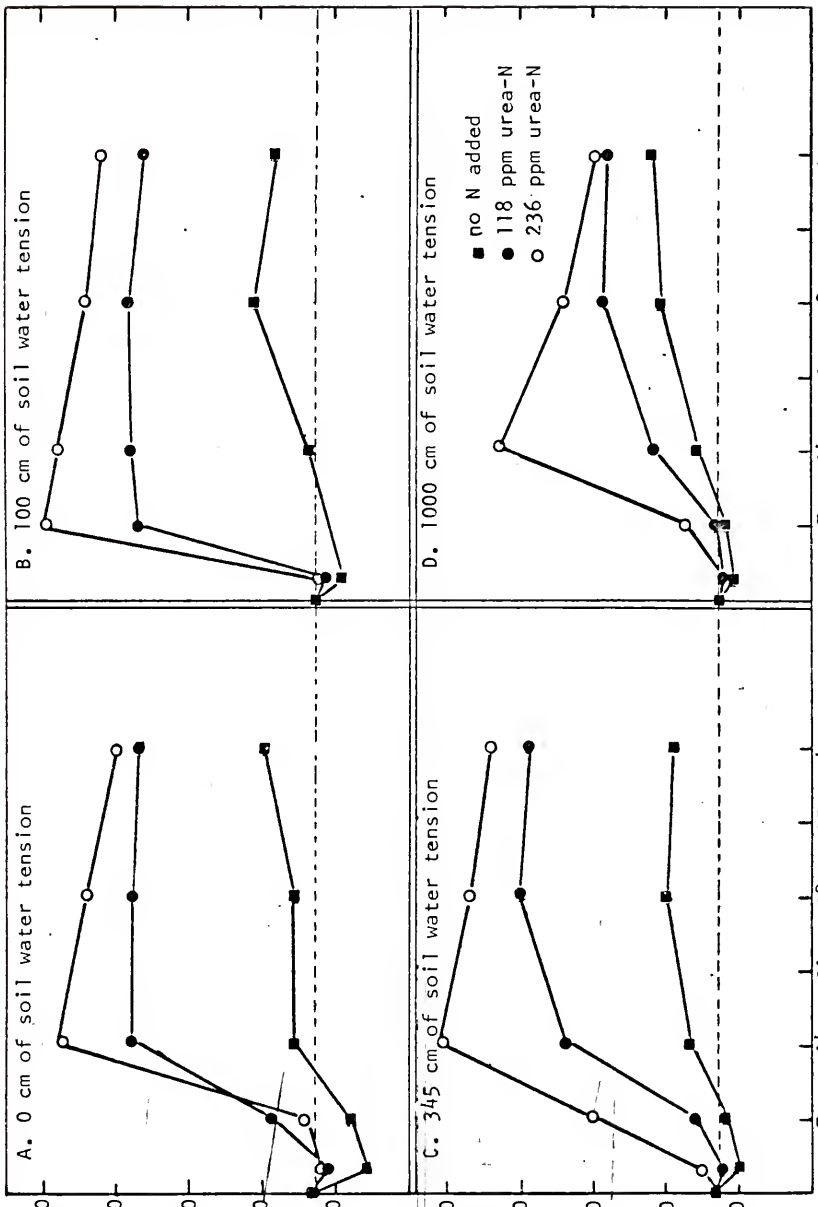


Fig. 10. The effects of soil moisture regimes, urea-N levels, and incubation period on soil pH.

longer incubation periods, pH increased up to 5.0. Under 100 cm of soil water tension (Fig. 10B), the drop in soil pH was only 0.1 unit but its rise occurred earlier (at the 28th day) and was greater (1.1 pH units). The patterns of soil pH changes in the unfertilized samples under 345 and 1000 cm of soil water tension (Fig. 10C and D) were essentially identical except that maximum pH rise under the latter was higher (5.2) than under the former (4.9).

Addition of urea-N generally did not cause the pH to rise until after 2 days of incubation. After 7 days of incubation under 0 and 1000 cm of soil water tension (Fig. 10A and B), soil pH increased slightly. Under 345 cm of soil water tension, additions of 236 ppm urea-N caused soil pH to rise to 6.0, while 118 ppm urea-N did not seem to cause any significant pH change (Fig. 10C). After 14 days of incubation, pH of the fertilized samples reached peak values under 0, 345, and 1000 cm of soil water tension. Maximum pH (8.1) was attained under 345 cm of soil water tension 14 days after the addition of 236 ppm urea-N. Towards the end of the experimental period, all pH values declined. Highest and lowest final soil pH values were detected under 345 and 1000 cm of soil water tension, respectively. In terms of individual pH profiles with respect to soil moisture regimes, soil pH peaked the highest under 345 and lowest under 1000 cm of soil water tension.

Experiment 2A. Lysimeter Pots with Two-year-old Slash Pine

Statistical analysis of the data collected in Experiment 2A are shown in Table 7A. Variables significantly affected by N treatments within each soil moisture regimes are shown in Table 7B. Under the high soil moisture regime (170 cm of water), 224 and 448 kg N/ha as $(NH_4)_2SO_4$ and 488 kg N/Ha as $(NH_2)_2CO$ effected higher Ca uptake than

Table 7. Statistical analysis of parameters measured in Experiment 2A: Lysimeter pots with two-year-old slash pine

A. Significance of the effects of soil moisture regimes and fertilizer treatments on slash pine growth response and soil parameters

Parameters	Soil moisture regimes (W)[a]	N fertilizer treatments (T)[b]	W x T
Growth response			
Height	**	**	NS
Diameter	**	**	NS
Dry weight	**	**	NS
Nutrient uptake			
N	*	**	NS
P	*	**	NS
K	NS	**	NS
Ca	**	**	*
Mg	NS	**	NS
Leaching losses			
NH_4-N	*	**	NS
NO_3-N	NS	**	NS
P	NS	**	NS
K	**	**	**
Ca	*	**	NS
Mg	NS	**	NS
Soluble salts	NS	**	*
Leachate pH[c]			
1	*	**	**
2	NS	**	NS
3	NS	**	NS
Residual Nutrients			
N	NS	NS	NS
KCl-ext. N	NS	NS	NS
P	**	**	*
K	NS	*	NS
Ca	NS	**	NS
Mg	NS	NS	NS
Final soil pH	NS	NS	NS

Table 7. continued.

B. The effects of il moisture regimes and ertilizer treatments on Ca uptake, eaching, residual P, and achate pH

Parameters	C	Soil moisture regime (cm of water) 170 U1	S1	U2	S2	500	U1	S1	U2	S2
Ca uptake (mg)	232b[e]	418ab	486a	526a	53(	)b	499a	290b	325ab	273b
K leaching (mg)	202a	100a	135a	175a	131	8b	138b	2[illegible]a	137b	308a
Residual P (mg)	93a	91a	74a	106a	76	36b	131[illegible]	[illegible]	163a	86b
Leachate pH 1	5.4b	6.2a	3.9c	5.9a	3.7c	.8ab	5.2a	4.4b	4.6b	4.2b

C. The effects of soil moisture regimes on slash pine growth response, nutrient uptake, leaching, and retention, and leachate pH

Parameters	Soil moisture regimes (cm of water) 170	500	Level of significance (F test)
Growth response			
Height (cm)	15.5	8.4	**
Diameter (mm)	6.8	4.7	**
Dry weight (g)	180.0	124.0	**
Nutrient uptake (mg)			
N	850	716	*
P	148	122	*
K	273	226	*
Ca	439	321	**
Mg	129	110	*
Leaching losses			
NH_4-N (%)[d]	7.4	9.0	*
K (mg)	149	218	**
Ca (mg)	819	719	*
Residual P (mg)	88	108	**
Leachate pH 1	5.0	4.6	*

Table 7. continued.

D. The effects of N fertilizer treatments on slash pine growth response, nutrient uptake, leaching, and retention, soluble salts, and leachate pH

Parameters	N fertilizer treatments 0	U1	S1	U2	S2
Growth response					
Height (cm)	8.0b	15.4a	9.9b	15.6a	10.9b
Diameter (mm)	2.3c	6.8ab	5.7b	7.7a	6.0b
Dry weight (g)	82c	182ab	138b	197a	161ab
Nutrient uptake (mg)					
N	316c	918ab	715b	1098a	868ab
P	80b	164a	133a	162a	138a
K	175c	310a	218bc	310a	312bc
Ca	211b	458a	388a	439a	403a
Mg	67c	161a	103bc	168a	100bc
Leaching losses					
NH_4-N (%)	0.11d	1.76d	10.70b	5.90c	22.60a
NO_3-N (%)	0.22c	0.76bc	0.52bc	2.52a	1.04b
P (mg)	254a	121b	212a	111b	261a
K (mg)	205a	119b	216a	156ab	220a
Ca (mg)	712cd	574de	949b	483e	1128a
Mg (mg)	282a	216b	274a	153c	260ab
Soluble salsts (g)	3.6c	3.2c	7.4b	3.6c	10.1a
Leachate pH					
1	5.1a	5.7a	4.1b	5.2a	4.0b
2	4.5a	4.7a	3.8b	4.2ab	3.7b
3	5.6a	5.4a	4.7b	5.0ab	4.4b
Residual nutrients (mg)					
P	89bc	111b	75c	135a	81c
K	109a	89ab	65b	88ab	68b
Ca	3534a	3610a	2451b	2914ab	2453b

[a]Soil moisture regimes: 170 and 500 cm of water.

[b]N fertilizer treatments: 0 = no N added; U1 = 224 kg N/ha as urea; S1 = 224 kg N/ha as ammonium sulfate; U2 = 2 x U1; S2 = 2 x S1.

[c]pH of leachates collected at different times after fertilization: 1 = 1 week, 2 = 8 weeks, 3 = 9 months.

[d]NH_4-N and NO_3-N are expressed as percent of the total initial N content of the soil.

[e]Differences in letters across each parameter indicate significant differences (at .05 level) between means as indicated by Duncan Multiple Range test.

the controls (no N treatment). Addition of $(NH_2)_2CO$ at the rate of 224 kg N/ha did not cause any response in terms of Ca uptake. Under the low soil moisture regime (500 cm of water), addition of $(NH_2)_2CO$ at the rate of 224 kg N/ha resulted in higher Ca uptake than the addition of 224 or 448 kg N/ha as $(NH_4)_2SO_4$ or where no N was added. The effect of 448 kg N/ha under the same soil moisture regime was not different from the effects of the other treatments.

Leaching losses of K under the high soil moisture regime was not affected by N treatments. Significant variation, however, occurred under the low soil moisture regime where adding 224 or 448 kg N/ha as $(NH_4)_2SO_4$ resulted in higher leaching losses of K than adding either levels of N as $(NH_2)_2CO$. Without N additions the amount of K lost through leaching was less than the amount lost following $(NH_4)_2SO_4$ fertilization but it was not different from the losses resulting from $(NH_2)_2CO$ fertilization.

Leaching losses of soluble salts were higher resulting from the addition of 224 or 448 kg N/ha as $(NH_4)_2SO_4$ than as $(NH_2)_2CO$ under the high soil moisture regime. Under the same soil moisture regime, leaching losses of soluble salts were higher from pots to which $(NH_4)_2SO_4$ had been added than from the control pots or those that received $(NH_2)_2CO$.

The five N treatments did not differ in their effects on residual P under the high soil moisture regime. Under the low soil moisture regime, however, there was significantly higher soil retention of P with either 224 or 448 kg N/ha as $(NH_2)_2CO$ than with 224 or 448 kg N/ha as $(NH_4)_2SO_4$ or without N.

Variations in leachate pH were more distinct during the early part of the experiment. Under the high soil moisture regime, 224 and 448 kg N/ha as urea caused leachate pH to rise to 5.9 and 6.2, respectively,

Under the low soil moisture regime, only 224 kg N/ha as urea brought leachate pH higher than 5.0. On the other hand, addition of N as $(NH_4)_2SO_4$ caused leachate pH to reach as low as 3.7, particularly under the high soil moisture regime. Growth response (height, diameter, and dry weight production) and nutrient uptake (N, P. K, Ca, and Mg) were higher under the high than low soil moisture regime (Table 7C). The high soil moisture regime effected higher leaching loss of Ca while the low soil moisture regime favored higher leaching losses of NH_4-N and K. Leachate pH during the early part of the experimental period was generally higher under the high than low soil moisture regime.

Greater height growth response was observed on pots receiving $(NH_2)_2CO$ (Table 7D). Higher level of N (448 kg N/ha) as $(NH_2)_2CO$ was apparently needed to elicit greater diameter growth and dry weight production). Higher nutrient (N, P, K, Ca, and Mg) uptake was also observed on slash pine fertilized with $(NH_2)_2CO$.

Leaching losses of N generally increased with increasing level of N application but $(NH_4)_2SO_4$ favored much higher leaching losses of N than $(NH_2)_2CO$. Leaching losses of P, K, Ca, and Mg, on the other hand, were generally lower from pots receiving $(NH_2)_2CO$ than those receiving $(NH_4)_2SO_4$. The amount of soluble salts leached through pots fertilized with $(NH_4)_2SO_4$ was more than twice the amount lost from pots fertilized with $(NH_2)_2CO$.

The effect of $(NH_2)_2CO$ fertilization on leachate pH generally did not vary from the control. However, $(NH_4)_2SO_4$ fertilization caused a significant drop in leachate pH, especially 1 to 2 weeks after fertilization.

The data shown in Table 8 suggest that generally higher amounts of

Table 8. Leaching losses of soluble salts during a period of nine months from the lysimeter pots with two-year old slash pine fertilized with urea and ammonium sulfate under two soil moisture regimes

Days after fertilization	Soil moisture regimes (cm of water)									
	170					500				
	0[a]	U1	S1	U2	S2	0	U1	S1	U2	S2
	g									
7	0.51	0.31	2.23	0.53	2.89					
12	0.40	0.51	1.42	0.71	2.30					
24						0.39	0.41	1.23	0.61	1.77
58	0.50	0.62	0.56	0.90	0.78					
64	0.30	0.31	0.34	0.27	0.55					
65						1.60	1.51	3.76	1.27	5.64
67	0.91	0.70	1.29	1.01	1.47	0.15	0.15	0.40	0.11	0.56
73	0.61	0.25	0.38	0.21	0.30	0.68	0.62	1.33	0.64	2.01
113	0.10	0.10	0.16	0.08	0.08	0.13	0.14	0.31	0.06	0.33
134	0.05	0.03	0.05	0.02	0.06					
146	0.17	0.14	0.31	0.16	0.22	0.22	0.20	0.27	0.20	0.30
241	0.07	0.13	0.18	0.13	0.18	0.10	0.11	0.22	0.12	0.18
251	0.12	0.18	0.20	0.13	0.17	0.16	0.12	0.08	0.12	0.33
Total	3.74c	3.28c	7.12a	4.15c	9.00a	3.43c	3.26c	7.60b	3.13c	11.12a

[a]See footnote b, Table 7A.

soluble salts were detected in leachates collected from pots fertilized with $(NH_4)_2SO_4$ and these amounts were particularly high during the early part of the experiment. Soluble salts detected 65 days after fertilization were about 3 times more in the leachates collected from pots fertilized with $(NH_4)_2SO_4$ than those fertilized with $(NH_2)_2CO$. It was two weeks before two slash pine seedlings fertilized with 448 kg N/ha as $(NH_4)_2SO_4$ started to show symptoms of salt injury; the two seedlings eventually died. The data referred to above, however, could not be compared because variable time of leachate collection under each soil moisture regime made the data difficult to statistically analyze. Despite the inclusion of leaching data on soluble salts that occurred during the latter part of the experimental period, statistical analysis of the total leaching losses still showed that within each soil moisture regime, $(NH_4)_2SO_4$ fertilization resulted in significantly higher leaching losses of soluble salts than either the control or $(NH_2)_2CO$ fertilization.

Correlation analysis was performed to establish the relationship between growth response and nutrient uptake and leaching losses of nutrients and soluble salts (Table 9). Results indicate that growth response (height, diameter, and dry weight production) were positively correlated with uptake of N, P, K, Ca, and Mg but negatively correlated with leaching losses of of P, K, Ca, and Mg. Leaching losses of NO_3-N were positively correlated with diameter growth and dry weight production. Leaching losses of NH_4-N and soluble salts were not correlated with growth response.

Characterization of the distribution of N in the lysimeter system (Experiment 2A) is shown in Tables 10 and 11. Nitrogen that was measured in the uptake, leaching, and soil retention distribution was expressed as

Table 9. Relationships among growth response, nutrient uptake, and leaching losses of nutrients and soluble salts in Experiment 2A: Lysimeter pots with two-year-old slash pine

Dependent variables	Nutrient uptake[a]					Leaching losses[b]						
	UN	UP	UK	UC	UM	LNH	LNO	LP	LK	LC	LM	SS
	correlation coefficients											
Height (cm)	0.61**	0.72**	0.59**	0.67**	0.59**	-0.20	0.15**	-0.53**	-0.62**	-0.12	-0.23**	-0.25
Diameter (mm)	0.77**	0.69**	0.60**	0.68**	0.68**	0.17	0.41*	-0.50**	-0.57**	-0.08	-0.46*	-0.01
Dry weight (g)	0.92**	0.85**	0.84**	0.92**	0.86**	0.08	0.33*	-0.63**	-0.64**	-0.03	-0.37*	-0.08

[a]Nutrient uptake: UN, UP, UK, UC, and UM = uptake (mg) of N, P, K, Ca, and Mg, respectively.

[b]Leaching losses: LNH, LNO, LP, LK, LC, LM, and SS = leaching losses of NH_4-N (% of total initial N), NO_3-N (% of total initial N), P (mg), K (mg), Ca (mg), Mg (mg), and soluble salts (g), respectively.

*Significant correlation at .05 level.

**Significant correlation at .01 level.

Table 10. Distribution of N in the lysimeter system fertilized with urea and ammonium sulfate under two soil moisture regimes

N distribution	Soil moisture regimes (cm of water)									
	170					500				
	0[a]	U1	S1	U2	S2	0	U1	S1	U2	S2
	% of total initial N									
Uptake	6.8	15.2	14.4	17.0	16.1	7.1	17.3	10.7	15.2	9.2
Leaching	0.4	2.6	7.7	8.2	17.8	0.3	2.3	11.5	6.4	20.8
Residual	94.9	76.7	74.6	64.4	61.1	97.1	78.2	73.5	65.0	62.4
Unaccounted[b]	-2.1	5.5	3.3	10.4	5.0	-4.5	2.2	4.3	13.4	7.6

[a]See footnote b, Table 7A.

[b]Percent of original soil N plus added N (total initial N) unaccounted for after nine months. Negative sign indicates a gain of N by the soil. See footnote b, Table 11.

Note: Total rain input of N/pot: NH_4-N = 14.0 mg; NO_3-N = 15.0 mg.

Table 11. Distribution of N in the lysimeter system fertilized with urea and ammonium sulfate under two soil moisture regimes

N distribution	Soil moisture regimes (cm of water)									
	170					500				
	0[a]	U1	S1	U2	S2	0	U1	S1	U2	S2
	% of added N									
Uptake	-	74.8	71.0	50.4	47.6	-	85.2	52.8	45.2	27.3
Leaching losses	-	13.2	38.2	24.3	52.7	-	11.1	56.3	19.0	61.8
Gaseous losses[b]	-	27.1	16.2	30.8	14.8	-	10.8	21.1	39.8	22.5
Removal[c]	-2.1	3.1	5.2	1.8	5.1	-4.5	1.4	3.6	13.4	7.6

[a]See footnote b, Table 7.

[b]Based on the assumption that the item unaccounted for in Table 10 was due to gaseous losses as NH_3 volatilization and/or volatilization.

[c]Apparent depletion of native N which was determined by expressing as percent of the total initial N the amount of N taken up by the seedlings, leached, and apparently volatilized and/or denitrified in excess of the added N.

percent of the total initial N content of the soil (Table 10). Subtracting the sum of the three pathways from the total initial N and expressing the difference as percent of the latter would result in an unaccounted for item. Under the high soil moisture regime, such item varied in the following order: U2 U1 > S2 > S1 > 0. Under the low soil moisture regime, the order was U2 > S2 > S1 > U1 > 0. Negative values corresponding to the controls signify that the sum of the three measured pathways exceeded the total initial N. In Table 11, uptake and leaching losses of N and the item unaccounted for in Table 10 are expressed as percent of the added N. By assuming that most of the N unaccounted for was due to gaseous losses as NH_3 volatilization and/or denitrification, another item was calculated, the apparent depletion of the native N. This was done by expressing as percent of the total initial N, the amount of N taken up by the seedlings, leached, and apparently volatilized and/or denitrified in excess of the added N. Under this item, depletion of the native soil N resulting from N fertilization followed the following order: S1 > S2 > U1 > U2 > 0 and U2 > S2 > S1 > U1 > 0 under high and low soil moisture regimes, respectively. Again, this shows that N seemed to be gained by the unfertilized pots. Calculation using the amount of rain recorded (Table 3) and rain concentrations of NH_4-N and NO_3-N (see Note, Table 10) would indicate that N input due to rain could not account for the N gained by the unfertilized pots.

Experiment 2B. Lysimeter Pots with One-year-old Slash Pine

The lysimeter pots used in Experiment 2A were flat-bottomed and were, therefore, restrictive to downward water movement. Furthermore, the seedlings had been growing in the pots for 11 months before ferti-

lization treatments were added and an examination of a few pots showed that the pot soil volume was well colonized by the seedlings root, thus inhibiting downward water flow through transpiration and, perhaps, as a physical barrier by the root mass. Experiment 2B was, therefore, conducted to characterize nutient movement through a lysimeter system that provided less restriction to downward water flow than the system employed in Experiment 2A. Since the pots in experiment 2B were placed at two sides of the lysimeter pit which received varying degrees of shading, the latter was considered a variable in the data analysis.

Most of the variables measured in Experiment 2B were non-significant with respect to degree of shading (Table 12A). Among the growth response variables, only dry weight production was significantly affected. Other parameters affected by shading were K uptake and pH of leachate collected 6 months after fertilization. Leaching losses of Ca and pH of leachates 6 days and 6 weeks after fertilization were highly significantly affected by degree of shading..

Nitrogen fertilizer treatments significantly affected diameter growth, uptake of N and Mg, pH of leachates collected 6 days after fertilization, and final soil pH. On the other hand, addition of either $(NH_2)_2CO$ or $(NH_4)_2SO_4$ significantly affected K uptake, nutrient leaching losses, and pH of leachates collected 6 months after fertilization.

Dry weight production of seedlings grown on the shaded side of the lysimeter pit was slightly higher than those grown on the exposed side (Table 12B). Correspondingly, K uptake was higher by the shaded seedlings than by the exposed plants. On the other hand, leaching losses of Ca, as well as pH of leachates collected at different times

Table 12. Statistical analysis of parameters measured in Experiment 2B: Lysimeter pots with one-year-old slash pine

A. Significance of the effects of shading and N fertilizer treatments on slash pine growth response and soil parameters

Parameters	Degree of shading (S)[a]	Fertilizer treatments (N)[b]	S x N
Growth response			
Height	NS	NS	NS
Diameter	NS	*	NS
Dry weight	*	NS	NS
Nutrient uptake			
N	NS	*	NS
P	NS	NS	NS
K	*	**	NS
Ca	NS	NS	NS
Mg	NS	*	NS
Leaching losses			
NH_4-N[c]	NS	**	NS
NO_3-N	NS	**	NS
P	NS	**	NS
K	NS	**	NS
Ca	**	**	NS
Mg	NS	**	NS
Leachate pH[d]			
1	**	*	NS
2	**	NS	NS
3	*	**	NS
Final soil pH	NS	*	NS

Table 12. continued

B. The effects of shading on dry weight production, K uptake, Ca leaching, and leachate pH

Parameters	Shaded side	Exposed side	Level of significance
Dry weight (g)	32.2	20.2	*
Nutrient uptake (mg)			
K	109	62	*
Leaching losses (mg)			
Ca	474	573	**
Leachate pH			
1	5.3	6.4	**
2	4.6	5.5	**
3	4.3	4.6	*

C. The effects of N fertilizer treatments on diameter growth, nutrient uptake and leaching, and leachate pH

Parameters	Fertilizer treatments 0	U1	S1	U2	S2
Diameter (mm)	4.2b	8.0a	5.8ab	8.6a	8.2a
Nutrient uptake (mg)					
N	103b	280ab	142ab	318a	164ab
K	49b	168a	58b	103ab	50b
Mg	10b	32a	11b	21ab	14ab
Leaching losses					
NH_4-N (%)	0.5d	7.4c	15.1b	12.2bc	26.9a
NO_3-N (%)	1.0c	2.8b	1.6c	4.4a	1.5c
P (mg)	248a	177b	248a	164b	294a
K (mg)	310a	167b	328a	180b	290a
Ca (mg)	561a	352b	684a	360b	600a
Mg (mg)	414a	144c	152c	96c	208b
Leachate pH					
1	6.3a	6.1a	5.8ab	6.4a	4.6b
3	5.2a	4.4b	4.1b	4.6ab	3.9b

[a]The pots were placed at two sides of the lysimeter pit which received varying degree of shading. One side (shaded side) did not receive direct sunlight while the other side (exposed side) received direct sunlight during most of the day.

[b]Fertilizer treatment: 0 = no N added: U1 = 224 kg N/ha as urea; S1 = 224 kg N/ha as ammonium sulfate; U2 = 2 x U1; S2 = 2 x S1.

Table 12. continued

[c] NH_4-N and NO_3-N were expressed as percent based on total initial N content of the soil

[d] pH of leachates collected at different times after fertilization: 1 = 6 days, 2 = 6 weeks, 3 = 6 months.

after fertilization, were significantly higher from the exposed pots than the shaded pots.

There was no significant difference in diameter growth with respect to source of N. However, the control (no N added) resulted in less diameter growth than where N was added. Uptake of N and K was greater from the $(NH_2)_2CO$ than $(NH_4)_2SO_4$ source, but only the low rate of $(NH_2)_2CO$ significantly increased Mg uptake over the other treatments.

Addition of N as $(NH_4)_2SO_4$ caused higher leaching losses of NH_4-N while $(NH_2)_2CO$ fertilization resulted in more leaching losses of NO_3-N, although nitrification, in general, was low (Table 12C). Leaching losses of P, K, Ca, and Mg seemed to be minimized by $(NH_2)_2CO$ fertilization.

The effect of N treatment on leachate pH varied distinctly only in the leachates collected 6 days after fertilization. Addition of 224 and 488 kg N/ha as $(NH_2)_2CO$ caused soil pH to reach 6.3 and 6.4, respectively while 448 kg N/ha as $(NH_4)_2SO_4$ tended to maintain leachate pH at the level before fertilization.

In Experiment 2A, the nutrient uptake was generally greater than nutrient leaching losses while the reverse was true in Experiment 2B (Table 13 and 14). Residual N values were approximately identical in both experiments. While the unfertilized pots in Experiment 2A apparently gained N, all treatments in Experiment 2B resulted in net losses of N that could not be accounted for (Table 13). Table 14 expresses the N pathways as percent of the added N. On the shaded side, apparent gaseous losses were greater from $(NH_2)_2CO$ than from $(NH_4)_2SO_4$ fertilization. On the exposed side, however, variation in apparent gaseous losses followed the following pattern: U1 > S2 > U2 > S1. In terms of apparent N depletion, the potted soil that

Table 13. Distribution of N in the lysimeter system fertilized with urea and ammonium sulfate under direct (exposed) and indirect (shaded) sunlight

N distribution	Shaded side[a]					Exposed side				
	0[b]	U1	S1	U2	S2	0	U1	S1	U2	S2
	% of total initial N									
Uptake	2.6	7.4	2.8	8.6	2.6	2.5	4.0	3.0	2.4	3.1
Leaching	1.4	10.7	16.7	15.3	27.8	1.6	13.5	16.5	20.7	29.0
Residual	93.7	80.0	80.1	66.0	68.2	90.6	76.2	77.5	70.4	58.4
Unaccounted[c]	2.2	1.9	0.4	10.1	1.4	5.3	6.3	3.0	6.5	9.5

[a]See footnote a, Table 12A.

[b]See footnote b, Table 12A.

[c]See footnote c, Table 14.

Note: Rain nutrient input/pot: NH_4-N = 7.8 mg; NO_3-N = 8.5 mg; Total = 16.3 mg.

Table 14. Distribution of N in the lysimeter system fertilized with urea and ammonium sulfate under direct (exposed) and indirect (shaded) sunlight

N distribution	Shaded Side[a]					Exposed Side				
	0[b]	U1	S1	U2	S2	0	U1	S1	U2	S2
	----------% of added N----------									
Uptake	-	42.6	16.2	29.0	8.8	-	23.0	17.3	8.1	10.5
Leaching	-	61.6	95.5	51.7	94.2	-	77.7	93.6	69.9	97.8
Gaseous Losses[c]	-	10.9	2.3	34.1	4.7	-	36.2	17.3	21.9	32.2
Removal[d]	6.3	2.6	2.6	4.4	2.2	9.4	6.4	5.2	-0.1	12.1

[a]See footnote a, Table 12A.

[b]See footnote b, Table 12A.

[c]This is based on the assumption that the item unaccounted for in Table 18 was due to gaseous losses as NH_3 volatilization and/or denitrification.

[d]Apparent depletion of native N which was determined by expressing in % of the total initial N the amount of N taken up by the seedlings, leached, and apparently volatilized and/or denitrified in excess of the added N.

received no N apparently lost considerable amount of its native N. Depletion of native N in the shaded side did not seem to distinctly vary with respect to sources and levels of N added. In the exposed side, however, practically no N was lost from the native N content of the potted soil fertilized with 448 kg N/ha as $(NH_2)_2CO$. On the other hand, addition of 448 kg N/ha as $(NH_4)_2SO_4$ resulted in the highest amount of native N depletion.

Experiment 3. Greenhouse Soil Columns

Statistical analysis of the variables measured in Experiment 3 are shown in Table 15. Under the high soil moisture regime (170 cm of water), addition of 488 kg N/ha as urea did not cause significant NH_3-N volatilization. Under the low soil moisture regime, however, significant amount of NH_3-N was volatilized from the added urea-N. This pattern is better emphasized in Fig. 11. Significant amount of unhydrolyzed urea-N and NH_4-N leached through the fertilized columns under the high soil moisture but not under the low soil moisture regime.

The one variable affected by soil moisture regimes within each soil type is the leaching loss of NO_3-N (Table 15C). This variation occurred only in one soil type, Bladen, where the high soil moisture regime caused significantly higher loss of NO_3-N.

The effects of urea-N additions within each soil type are shown in Table 15D. Additions of urea at a rate equivalent to 448 kg N/ha caused significant reduction in non-extractable N; the greatest percent reduction appears to have occurred in the Leon soil and the least in the Plummer +D. Urea-N fertilization also caused a signi-

Table 15. Statistical analysis of parameters measured in Experiment 3: Greenhouse soil columns

A. Significance of the effects of soil moisture regimes, urea fertilization, soil types, and soil depths on soil parameters

Parameters	Soil moisture regimes (M)[a]	Urea-N added (N)[b]	Soil type (S)[c]	Soil depth	M x N	M x S	N x S
NH_3-N volatilile losses[d]	*	**	NS	-	*	NS	NS
Leaching losses							
Urea-N	*	**	NS	-	*	NS	NS
NH_4-N	**	**	NS	-	*	NS	NS
NO_3-N	**	NS	**	-	NS	**	NS
Non-ext. N[e]	NS	**	**	**	NS	NS	**
KCl-ext. N[f]							
NH_4-N	NS	**	**	**	NS	NS	*
NO_3-N	NS	*	**	*	NS	NS	NS
Org. N	NS	**	**	**	NS	NS	**
Final soil pH	NS	**	**	**	NS	NS	**

B. The effects of soil moisture regimes on volatilization and leaching losses of N

Parameters	Soil moisture regimes (cm of water)			
	170		500	
	0[g]	448	0	448
NH_3-N (%)	0.0a	0.54a	0.0b	4.20a
Leaching losses (%)				
Urea-N	0.0b	0.93a	0.0a	0.13a
NH_4-N	0.09b	0.21a	0.04a	0.07a

Table 15. continued.

C. The effects of soil types and soil moisture regimes on leaching losses of NO_3-N

Parameters	Soil types: Leon 170	Leon 500	Bladen 170	Bladen 500	Plummer 170	Plummer 500	Plummer + D 170	Plummer + D 500
Leaching losses of NO_3-N (%)	0.07a	0.06a	0.54a	0.08b	0.10a	0.02a	0.04a	0.02a

D. The effects of soil types and urea fertilization on non-extractable and KCl-extractable N and soil pH

Parameters	Soil types: Leon 0	Leon 448	Bladen 0	Bladen 448	Plummer 0	Plummer 448	Plummer + D 0	Plummer + D 448
Non-ext. N (%)	98.0a	73.7b	95.8a	83.1b	97.3a	92.7a	98.1a	92.3b
KCl-ext. N								
NH_4-N (ppm)	4.7a	93.4a	28.5a	156.9a	70.7b	270.2a	51.6b	423.3a
Org. N (%)	37.8a	4.8b	18.2a	2.4b	9.8a	2.8a	26.8a	1.8b
Final soil pH	4.6b	6.1a	4.5b	5.0a	3.7b	4.3a	3.7b	4.3a

Table 15. continued.

E. The effects of soil moisture regimes on N volatilization and leaching

Parameters	Soil moisture regimes (cm of water) 170	500	Level of significance
NH_3-N (%)	0.27	2.11	*
Leaching losses (%)			
Urea-N	0.46	0.06	*
NH_4-N	0.15	0.06	**
NO_3-N	0.19	0.04	**

F. The effects of urea fertilization on N volatilization and leaching, non-extractable N, KCl-extractable N, and soil pH

Parameters	Urea-N added (kg/ha) 0	448	Level of significance
NH_3-N (%)	0.0	2.4	**
Leaching losses (%)			
Urea-N	0.0	0.5	**
NH_4-N	0.07	0.14	**
Non-ext. N (%)	97.3	85.4	**
KCl-ext. N			
NH_4-N (ppm)	38.8	236.0	**
NO_3-N (ppm)	3.0	14.2	**
Org. N (%)	23.2	4.9	**
Final soil pH	4.1	4.9	**

Table 15. continued

G. The effects of soil types on N volatilization, non-extractable N, and KCl-extractable N

Parameters	Soil types			
	Leon	Bladen	Plummer	Plummer + D
Leaching losses (%)				
NO_3-N	0.06b	0.31a	0.06b	0.03b
Non-ext. N (%)	85.8b	89.5b	95.0a	95.0a
KCl-ext. N				
NH_4-N (ppm)	49.0c	92.7c	170.4b	237.4a
NO_3-N (ppm)	2.0b	13.0a	8.1a	11.4a
Org. N (%)	21.3a	10.3b	6.3b	14.3ab
Final soil pH	5.3a	4.7b	4.0c	4.0c

H. The effects of soil depths on non-extractable N, KCl-extractable N, and soil pH

Parameters	Soil depth (cm)		
	10	20	30
Non-ext. N (%)	87.0b	93.0a	94.2a
KCl-ext. N			
NH_4-N (ppm)	262.0a	88.0b	61.0b
NO_3-N (ppm)	11.9a	8.3ab	5.5b
Org. N (%)	20.1a	18.5a	0.0b
Final soil pH	4.8a	4.4b	4.3b

[a]Soil moisture regimes (cm of water): 170 and 500.

Table 15. continued.

[b]Urea-N added: 0 and 448 kg/ha.

[c]Soil types: Leon fs, Bladen sl, Plummer fs, and Plummer + D (see footnote e, Table 1).

[d]Percent values of NH_3-N and leaching losses of N are based on total initial N content of the soil.

[e]Non-extractable N is expressed as percent of the total N content of the soil.

[f]KCl-extractable NH_4-N and NO_3-N are expressed as ppm. KCl-extractable organic N is expressed as percent of the total KCl-extractable N.

[g]See footnote b above.

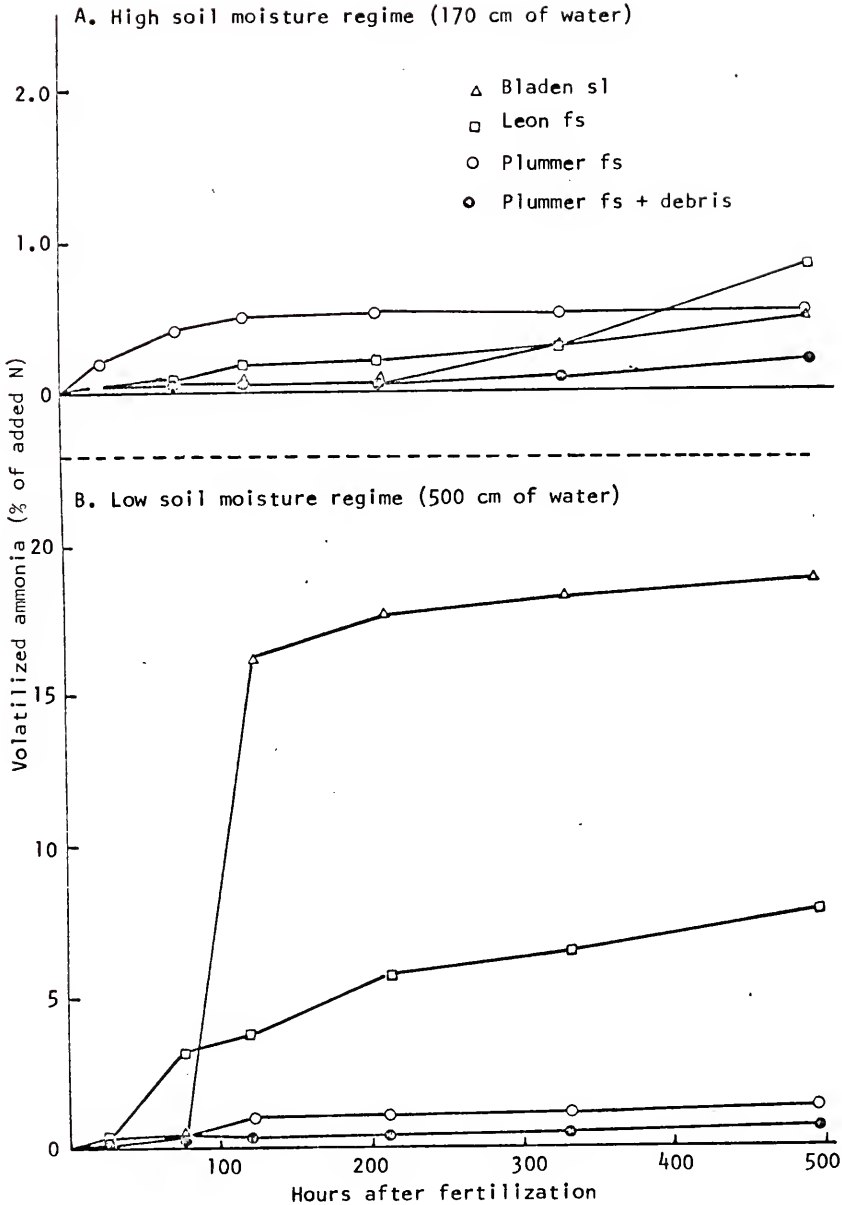


Fig. 11. Accumulative volatilization losses of ammonia from urea applied to three forest soil types under two soil moisture regimes.

ficant decrease in the amount of KCl-extractable organic N. The greatest percent decrease also occurred in the Leon soil while the least occurred in the Bladen soil. Final soil pH increased in all soil types resulting from urea-N fertilization.

The effects of soil moisture regimes are shown in Table 15E. Allowing the soil moisture potential to approach 500 cm of water or delaying the addition of water to the designated columns 1 week after fertilization caused a significant amount of NH_3-N to volatilize from the added N. On the other hand, maintaining soil moisture regimes within the range of 0 to 170 cm of soil water tension promoted significant leaching losses of unhydrolyzed urea-N, NH_4-N, and NO_3-N.

Means of parameters significantly affected by urea-N treatment are shown in Table 15F. The addition of 448 kg N/ha as urea resulted in the following: 1) more NH_3-N volatilization and leaching loss of unhydrolyzed urea-N and NH_4-N, 2) less non-extractable and KCl-extractable organic N remaining in the soil, 3) more KCl-extractable NH_4-N and NO_3-N, and 4) higher final soil pH.

Means of parameters significantly affected by soil types are shown in Table 15G. Leaching losses of NO_3-N were significantly higher in the columns filled with Bladen soil than in any of those filled with the other soil types. Residual, non-extractable N was lower in Leon or Bladen than in Plummer or Plummer + D. Apparent mineralization relative to the total N content was slightly greater (although not significantly) in Leon than in Bladen. Highest KCl-extractable NH_4-N was obtained from Plummer + D while least was obtained from Leon; intermediate amounts were obtained from Plummer and Bladen. Leaching losses of NO_3-N from columns filled with Bladen,

Plummer, and Plummer + D did not significantly vary but leaching losses from those filled with Leon were significantly less. In terms of KCl-extractable N, relatively more organic N was removed from the Leon than from Bladen or Plummer soils. Final soil pH was highest in Leon, second highest in Bladen, and lowest in Plummer + D.

Significant depletion of the non-extractable N appears to have occurred in the upper 10 cm of the soil collumns. KCl-extractable N and final soil pH were similarly higher in the upper than lower sections of the soil columns.

Experiment 4. Laboratory Soil Columns

Results of Experiment 4 suggest that important consequences of urea-N applications occurred during the first few days after fertilization. Data in Experiment 3 also indicate that intense chemical and biological activity was concentrated at the upper 10-cm layer of the soil columns. Experiment 4, therefore, was undertaken to characterize these consequences on a short-time scale.

Statistical analyses of the data in Experiment 4 are shown in Table 16A. The reduction in the amount of NH_4-N and NO_3-N lost through leaching occurred only in the Leon soil (Table 16B). In this soil, more urea-N was leached after 5 than 2 days following fertilization (Table 16C). More NH_4-N was leached from the Plummer or Plummer + D soil columns 5 days than 2 days after fertilization. On the other hand, it was only in the Leon soil that sampling time significantly affected leaching loss of NO_3-N.

In the Plummer soil column, more unhydrolyzed urea-N was extracted from the lower than the upper half of the columns while the reverse was true in the Plummer + D (Table 16D). Greater amounts of KCl-

Table 16. Statistical analysis of parameters measured in Experiment 4: Laboratory soil columns

A. Significance of the effects of soil types, PMA, sampling time, and soil depths on leachate and soil pH and KCl-extractable and leachable N

Parameters	Soil types (S)[a]	PMA[b]	Days (D)[c]	Soil depth (L)[d]	SxPMA	SxD	SxL
Leaching losses (% of added N)							
Urea-N	**	**	**	-	NS	**	-
NH_4-N	*	*	NS	-	**	NS	-
NO_3-N	**	*	NS	-	**	NS	-
Leachate pH	**	*	NS	-	**	NS	-
KCl-ext. N (% of added N)							
Urea-N	**	NS	**	NS	NS	*	**
NH_4-N	**	NS	*	*	NS	*	NS
NO_3-N	**	NS	NS	**	NS	*	**
Final soil pH	**	**	**	NS	**	NS	NS

B. The effects of soil types and PMA treatments on N leaching losses and leachate and soil pH

	Soil types							
	Leon		Bladen		Plummer		Plummer + D	
Parameters	0[b]	50	0	50	0	50	0	50
Leaching losses (% of added N)								
NH_4-N	5.5a	0.3b	0.5a	0.6a	1.1a	1.3a	2.3a	2.0a
NO_3-N	0.3a	0.04b	0.02a	0.02a	0.03a	0.02a	0.05a	0.05a
Leachate pH	8.0a	5.2b	5.2a	4.5a	4.2a	4.0a	4.3a	4.2a
Soil pH	7.7a	4.3b	6.4a	5.7a	5.7a	5.1a	5.0a	4.9a

Table 16. continued.

C. The effects of soil types and sampling time on leaching losses of urea-N and KCl-extractable N

	Soil types							
	Leon		Bladen		Plummer		Plummer + D	
Parameters	2[c]	5	2	5	2	5	2	5
Leaching losses (% of added N)								
Urea-N	61.10a	26.58b	48.65a	38.58a	23.00a	14.25a	9.70a	6.90a
KCl-ext. N (% of added N)								
NH_4-N	2.48a	4.10a	5.35a	6.70a	13.85b	27.58a	39.62b	75.60a
NO_3-N	0.08a	0.10a	0.20a	0.00b	0.30b	1.22a	1.12a	0.81b

D. The effects of soil types and depths on KCl-extractable N

	Soil types							
	Leon		Bladen		Plummer		Plummer + D	
Parameters	5	10	5	10	5	10	5	10
KCl-ext. N (% of added N)								
Urea-N	0.05a	0.10a	0.57a	1.04a	0.34b	1.34a	1.11a	0.39b
NH_4-N	2.35a	4.22a	7.00a	5.05a	45.68a	15.75b	75.98a	39.25b
NO_3-N	0.15a	0.02b	0.10a	0.10a	1.08a	0.40b	1.65a	0.25b

Table 16. continued

E. The effects of soil types on leachable and KCl-extractable N and leachate and soil pH

Parameters	Soil types			
	Leon	Bladen	Plummer	Plummer + D
Leaching losses (% of added N)				
Urea-N	43.8a	44.1a	18.6b	8.3c
NH_4-N	2.9a	0.6b	1.2a	2.2a
NO_3-N	0.16a	0.02b	0.02b	0.05b
Leachate pH	5.6a	4.9ab	4.1b	4.2b
KCl-ext. N (% of added N)				
Urea-N	0.07b	0.81a	0.84a	0.75a
NH_4-N	0.32c	0.60c	3.06b	4.54a
NO_3-N	0.008b	0.010b	0.070a	0.100a
Final soil pH	6.5a	6.0a	5.4b	5.0b

F. The effects of PMA treatment on N leaching losses and leachate and soil pH

Parameters	PMA added (ppm)		Level of significance
	0	50	
Leaching losses (% of added N)			
Urea-N	21.6	35.8	**
NH_4-N	2.4	1.0	*
NO_3-N	0.09	0.03	*
Leachate pH	5.4	4.4	*
Final soil pH	6.2	5.3	**

Table 16. continued.

G. The effects of sampling time on leachable and KCl-extractable N and soil pH

Parameters	Days after fertilization 2	5	Level of significance
Leaching losses (% of added N)			
Urea-N	39.5	17.9	**
KCl-ext. N (% of added N)			
Urea-N	0.94	0.30	**
NH_4-N	1.53	2.74	*
Final soil pH	5.3	6.2	**

H. The effects of soil depths on KCl-extractable N

Parameters	Soil depth (cm) 5	10	Level of significance
KCl-ext. N (% of added N)			
NH_4-N	0.26	1.61	*
NO_3-N	0.07	0.02	**

[a]Soil types: Leon fs, Bladen sl, Plummer fs, and Plummer + D.

[b]PMA = phenylmercuric acetate added at two levels: 0 and 50 ppm.

[c]The columns were sampled twice, at 2 and 5 days after fertilization.

[d]Soil depth in cm.

extractable NH_4-N, however, were found in the upper than lower half of the Plummer or Plummer + D soil columns. Except for the Bladen soil, more NO_3-N was extracted from the upper than the lower half of all the soil columns.

Leaching losses of unhydrolyzed urea-N were higher from Leon or Bladen soil than from Plummer or Plummer + D (Table 16E). Leaching losses of NH_4-N and NO_3-N were generally less from the Bladen than from the other soils. The rise in pH of leachates collected from the columns filled with leon was higher than those collected from columns filled with Plummer or Plummer + D. Retention (KCl-extractable) of unhydrolyzed urea-N was less in the Leon soil than in any of the other soil types. KCl-extractable NH_4-N and NO_3-N were lower in Leon or Bladen than in either Plummer or Plummer + D; significantly higher amount of NO_3-N was extracted form Plummer + D than from Plummer. Final soil pH values were higher in Leon or Bladen than Plummer or Plummer + D.

Variables significantly affected by PMA treatment are shown in Table 16F. Additions of PMA resulted in higher leaching losses of unhydrolyzed urea-N, less leaching losses of NH_4-N and NO_3-N, and less change in leachate and final soil pH.

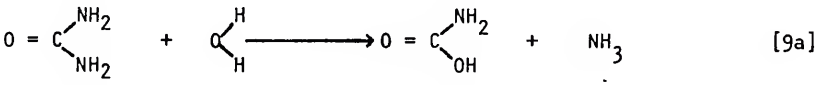
DISCUSSION

Ureolysis

The distinctive influence of soil moisture on the disappearance of unhydrolyzed urea-N in a Leon soil in Experiment 1 (Fig. 8) underscores the essentiality of water in the hydrolysis of urea. When the soil was kept close to saturation (Fig. 8A), anerobic condition may have slowed down the activity of the ureolytic microorganisms. This is evidenced by the drop in hydrolytic rate during the 7- to 14-day period following urea-N application. Since the culture medium used in Experiment 1 was selective for aerobic or facultative microorganism, the ureolytic groups that were isolated and identified were, therefore, aerobic or facultative. The predominant microbial groups isolated and identified are fungi (Note, Table 5). A good soil moisture supply is required by fungi for high activity in the soil but when soil moisture is excessive, their activity is slowed down, if not stopped (Alexander, 1961). The bacterial groups enumerated by Alexander (1961) as ureolytic are: Bacillus (aerobic, sometimes facultative), Pseudomonas (aerobic), Corynebacterium (aerobic), Actinomycetes (predominantly aerobic), and Clostridium (anaerobic).

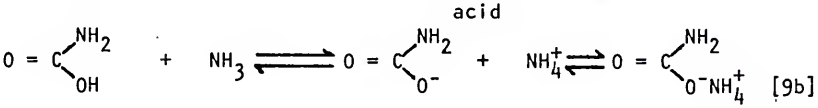
In spite of probable anaerobic conditions under 0 cm of soil water tension, however, hydrolysis of urea proceeded at a faster rate after 14 days (Fig. 8A). This suggests that hydrolysis of urea is not solely dependent on the presence or activity of the ureolytic microorganisms. The continued operation of urea hydrolysis under such conditions may be due to two possible processes. One is the hydrolytic

power of water. Each water molecule may act as a nucleophile and attack the carbonyl group of each urea molecule and result in the displacement of one amide of urea by a hydroxyl and the production of NH_3 and carbamic acid (Manziek, 1974, personal communication). The presence of NH_3 provides an electronegative pull which causes carbamic acid (NH_2COOH) to dissociate resulting in the formation of ammonium carbamate. The following reactions summarize the process.



[9a]

(urea) (water) (carbamic acid) (ammonia)



[9b]

Eq. [9b] is reversible and therefore dependent on the concentration of urea and/or supply of soil moisture. The hydrolytic power of water can be expected to be greater when the urea concentration is low because the nucleophile/carbonyl ratio is high. The disappearance of urea through the simple action of water under saturated soil condition is, therefore, a distinct possibility.

The other possible process by which hydrolysis proceeded under saturated condition was by the aciton of exogenous enyzme urease. Paulson and Kurtz (1969, 1970) showed that the hydrolytic activity of soil is primarily due to extracellular urease that exists freely or in complex forms with the soils colloids. In the presence of urease and water, reactions shown in Eqs. [1], [2], and [3] would proceed. It is reasonable to believe that the ureolytic process indicated in Fig. 8A was due to the availability of water and urease, which resulted in

hydrolysis of urea in spite of the effect of anaerobism on the ureolytic microbes.

Ureolysis was more rapid under 100 cm of soil water tension than other moisture conditions in Experiment 1 (Fig. 8B). This soil moisture potential limit corresponded to a maximum water content of 5.4 % by weight, a condjtion which indicated optimal aeration and therefore favorable environment for aerobic microorganisms. Gould et al. (1973) reported that endogenous urease hydrolyzed urea faster than exogenous or clay-adsorbed urease. This was probably because exogenous urease is likely to lose its activity with age and clay-adsorbed urease may have altered its configuration in such a manner that its reactive sites were deactivated. Gould et al. (1973) also reported that over an application range of 0 to 800 ppm urea-N, the hydrolytic rate of Alberta soils were linear with urea-N concentrations. Population of ureolytic microorganisms increased in response to levels of urea-N added (Table 5). That the extracts used in the plating experiment were obtained from samples incubated for 1 week under 100 cm of soil water tension would seem to indicate that the ureolytic microorganism that were identified (Note, Table 5) most probably exerted a predominant influence on the rapid rate of urea disappearance.

The results in Experiment 4 (Table 16) provide further evidence of the importance of microbial activity in the hydrolysis of urea. Bremner and Douglas (1971) found that of the 15 urease inhibitors tested, PMA was the second most effective. That the addition of 50 mg of PMA/g of soil in Experiment 4 resulted in significantly higher leaching losses of unhydrolyzed urea-N would seem to indicate that PMA significantly retarded microbial action on urea such that more of the

latter became available for leaching. The greater effectiveness of PMA in Leon than in Bladen or Plummer soils suggest that PMA inhibition of urease activity was affected by organic matter or clay content of the soil. Bailey and White (1964) and Barrows (1966) reported that in general activity of biocides is lowest in soils with high organic matter or clay content.

Soil types showed some influence on ureolytic rate. Table 16C shows that more unhydrolyzed urea-N was recovered from Leon and Bladen than the Plummer and Plummer + D columns. It was expected that leaching of urea-N from the Bladen sandy loam would be lower than from the Leon fine sand. This apparently contradicting result seems to reflect the difficulty of handling fine textured soil samples in columns. They either pond for a sustained period after water addition or else channel along the PVC-soil interface. Slightly more urea-N was leached from the Plummer than the Plummer + D column. The difference in the organic matter contents between the two soil samples probably played a role in the rate of urea hydrolysis. According to Gould (1973), activity of ureolytic microorganisms is enhanced by high organic matter content of the soil.

Ammonification

In Experiments 1 through 4, ammonification appears to be the predominant transformation pathway of urea-N. This conforms with the report of Smith et al. (1971) and Beaton (1973) that production of NH_4-H is the predominant process that follows the addition of urea-N to acid forest soils.

In Experiment 1, soil moisture potentials and incubation periods had distinct influences on the production of NH_4-N after fertilizing

a Leon soil with urea. The trends in the ureolytic and ammonification curves (Fig. 8) seem to indicate that ammonification closely followed the hydrolysis of urea. Under 0 or 100 cm of soil water tension, the occurrence of maximum NH_4-H production coincided with the complete disappearance of urea-N (Fig 8A and 8B). Subsequent to peak production, ammonification generally declined after urea was completely hydrolyzed or when its hydrolytic rate declined. This underscored the dependence of ammonification on urea as its main substrate in these tests. After the consumption of the main substrate, the amount of NH_4-N detected in the soil may be a function of nitrification and/or volatilization. Leaching losses of NH_4-N measured in Experiment 2A, 2B, and 3 also indicate the importance of the ammonification process following urea fertilization (Tables 7, 12, and 15).

Leaching losses of NH_4-N, in general, was significantly reduced by PMA treatment (Table 16F), an indication that the production of NH_4-N was limited by the inhibition of ureolysis by PMA. With respect to soil types, ammonification was minimum in the Bladen soil (Table 16E). When the soil type-PMA treatment interaction is evaluated (Table 16B), it was only in Leon that PMA treatment significantly reduced apparent ammonification. This would seem to indicate that PMA also inhibited ammonification under the influence of organic matter and clay content of the soil (Bailey and White 1966; Barrows, 1966).

Nitrification

After reaching peak levels resulting from the addition of urea-N, the production of NH_4-N started to decline (Fig. 8). Correspondingly, NO_3-N accumulation resulting from the same N treatments began to rise (Fig. 9). On the other hand, when NO_3-N accumulation declined after

reaching a peak level, NH_4-N production resumed its upward trend. This interplay of NH_4-N and NO_3-N production or accumulation strongly indicates that the amount of NH_4-N detected in the soil was partially a function of nitrification. The oscillating pattern of the nitrification curves, especially those under 0 and 100 cm of soil water tension, suggests that availability of substrate was not the only controlling factor of the nitrification process characterized in Experiment 1. Change in soil pH probably influenced the observed pattern of nitrification. Within 14 days, the soil pH in Experiment 1 increased from 4.3 to 7.8, 8.1, and 7.3 under 0, 100, 345, and 1000 cm of soil water tension, respectively. During the period from 14 to 42 days, pH did not drop appreciably. It is possible that the NO_3-N detected at peak levels on the 28th day of incubation was formed shortly after the 14th day when the nitrifying microorganisms were not yet severly affected by pH. Martin et al. (1943) reported that pH 7.7 is the critical point beyond which conversion of NO_2-N to NO_3-N ceases. It is, therefore, probable that high soil pH led to the accumulation of NO_2-N which is more toxic to Nitrobacter than to Nitrosomonas (Alexander, 1961; Fiedler, 1971; Olson et al., 1971). Aside from being toxic to Nitrobacter, the NO_2-N that accumulated may have led to denitrification loss. It is also possible that the NH_3-N that generated the high pH may have been toxic to the nitrifiers.

Nitrification in the unfertilized samples declined with increasing length of incubation period. This appears to be a function of the decreasing availability of NH_4-N as a substrate.

In Experiment 2A, 224 kg N/ha as urea or $(NH_4)_2SO_4$ did not produce significantly greater amount of NO_3-N than the control (Table 7D).

Increasing the N application rate to 448 kg N/ha as urea or $(NH_4)_2SO_4$, however, resulted in higher NO_3-N production with the former eliciting the highest amount of NO_3-N production. With an application rate of only 224 kg N/ha as urea or $(NH_4)_2SO_4$, plant uptake of NH_4-N may have reduced the amount of NH_4-N available for conversion to NO_3-N. Soil moisture regime did not affect nitrification in Experiment 2A. Probably, all NO_3-N formed in the soil between leachings moved along each leaching front regardless of irrigation or rainfall frequency or volume. In Experiment 2 B, apparent nitrification was also higher resulting from the addition of 448 kg N/ha as urea (Table 12C). Leaching losses of NO_3-N in Experiment 2B were generally higher than those in Experiment 2A. In Experiment 2A, fertilization was done 10 months after the seedlings were planted in the pots. During this period, plant uptake may have reduced NH_4-N available for nitrification or any NO_3-N formed during the early part of the ten-month period may have been lost through leaching. In Experiment 2B, fertilization was done about 2 weeks after the soil was placed in the lysimeter pots and planted to slash pine. The fallow condition of the soil in Experiment 2B may have favored higher nitrification rate. Lower rate of NH_4-N uptake by the newly planted seedlings may also have provided greater available NH_4-N as a nitrification substrate.

The accumulative amount of NO_3-N detected in the leachate in Experiment 2A, together with the changes of the leachate pH with time, is shown in Fig. 12. The significantly greater amount of NO_3-N due to the addition of 448 kg N/ha as urea is well emphasized. When the

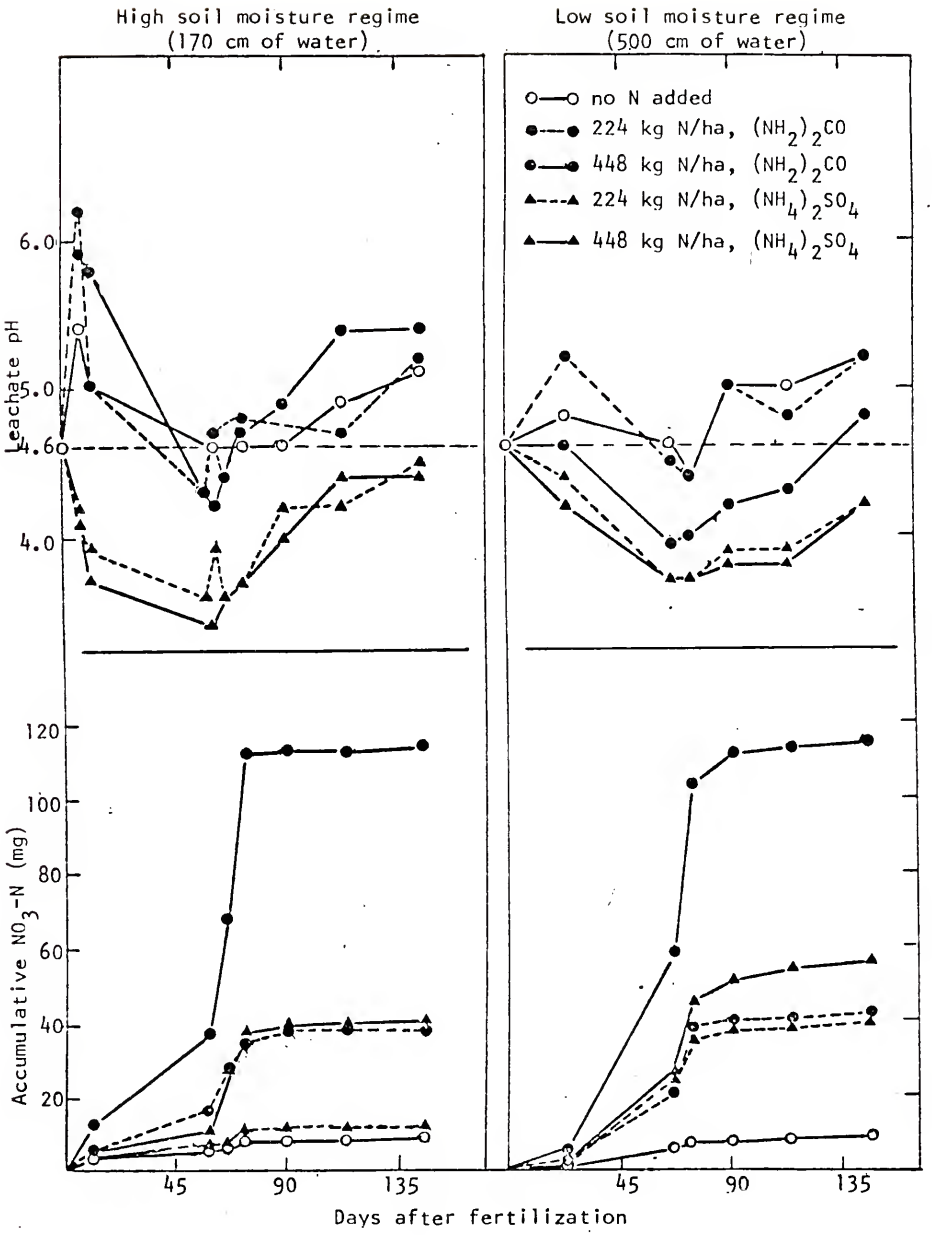


Fig. 12. The effects of urea and ammonium sulfate fertilization of potted slash pine under two soil moisture regimes on leachate pH and leaching losses of nitrate-N.

increased. This pattern conforms with the fact that nitrification is an acidifying process; each mole of NH_4-N oxidized to NO_2 or NO_3 liberates four protons.

In Experiment 3, NO_3-N losses through leaching were significantly affected by soil moisutre regime; more NO_3-N was detected in the leachates collected from columns under the high soil moisutre regime (Table 15E). Further examination of the soil type-soil moisture regime interaction shows that such significant effect occurred only in the Bladen soil (Table 15C). It is possible that Bladen had a higher population of nitrifying microorganisms which were stimulated by favorable moisture conditions. That the highest amount of KCl-extractable NO_3-N was obtained from Bladen, although not significantly higher than from Plummer or Plummer + D, would seem to explain the above variation in NO_3-N leaching losses.

In Experiment 4, the highest leaching loss of NO_3-N occurred in the Leon and lowest in the Bladen soil. Furthermore, KCl-extractable NO_3-N in Experiment 4 was significantly lower in Bladen than in Plummer or Plummer + D (Table 16E). There are three possible explanations for such contradictory results in nitrification in Experiment 3 and 4. One is that Experiment 4 was carried on only for 5 days while Experiment 3 was carried on a 26-day duration. Time may have been too short for the microbial population to become fully stimulated in Experiment 4. The second possibility is that the PMA treatment may have adversely affected the nitriflers more in Bladen than in Plummer or Plummer + D. The third possible explanation is that Experiment 4 was carried out in the laboratory where the temperature was lower (23 C) than in the greenhouse (up to 30 C).

Volatilization

The reported inefficiency of urea as a fertilizer has been commonly attributed to volatilization of NH_3 gas (Volk, 1966; Watkins et al., 1972; Power, 1974). Many techniques have been devised to monitor NH_3 evolved from urea added to and hydrolyzed in the soil. Two techniques were used in this study to determine NH_3 volatilization from urea applied to selected forest soils of the Southeastern Coastal Plain. One was by acidified NH_3 sorber method and the other was the N recovery method (Nommik, 1973b).

The acidified sorber method was employed in Experiment 3. Results indicated that the amount of NH_3 that apparently volatilized varied with soil moisture regime (M), urea-N treatment (N), and M X N interaction (Table 15A). Analysis of the variability Table 15B) revealed that it was only under the low soil moisture regime (500 cm of soil water tension) that significant amount of NH_3 was evolved from the added urea-N. Many investigators (Kresge and Satchell, 1960; Gasser, 1964; Volk, 1966; Fiedler, 1971) have observed that rapid rate of NH_3 volatilization occurs during the drying cycle of the soil. The longer the cycle the more volatilization of NH_3. Another reason for the high rate of NH_3 volatilization under the low moisture conditions was the manner in which the high soil moisture regime (170 cm of soil water tension) was maintained. Under the high soil moisture regime, the predetermined soil moisture potentials were approached in 1 to 3 days after fertilization. During this period, considerable amount of unhydrolyzed urea may have still remained in the soil and the addition of distilled water instantaneously to bring soil moisture potentials down to 0 cm of soil water tension may have removed the compound from the volatilization zone. Detection of unhydrolyzed urea in the leachate

under the high, but not under the low, soil moisture regime would seem to bear out this point.

Although the analysis of variance did not indicate a significant interaction between soil types and soil moisture regimes, Fig. 11 reveals some interesting features of this interaction. Under the high soil moisture regime (Fig. 11A), NH_3 volatilization from Plummer was higher during the early stage of the experiment. This would seem to indicate that hydrolysis of urea occurred earlier in this soil under high soil moisture conditions. During the latter part of the experiment, volatilization rate from Leon soil became higher than the rest. Hydrolytic activity in this soil probably did not start as early as in the Plummer or else the ureolytic microorganisms in the Leon soil were less active than those in the Plummer soil. Furthermore, when the ureolytic microorganism were already stimulated, leaching of unhydrolyzed urea-N deprived such organism of substrate.

Fig. 11B shows that after 4 days, volatilization of NH_3 from the Bladen columns amounted to as much as 16.5 % of the added urea-N and continued to rise at small increments until the end of the experiment. Volatilization of NH_3 from Leon occurred earlier than from Bladen, but its total was only 8 % of the added urea-N. These two results are surprising because it was expected that NH_3 volatilization from the Bladen soil would be less than from the Leon because the former has greater CEC than the latter (Table 1). Furthermore, the higher clay and organic matter content of the Bladen than the Leon soil should have prevented volatilization by the mechanism proposed by Greenland (1965), McLaren and Peterson (1965), and Mitsui (1967). The method used in watering the soil columns and low infiltrability may have resulted in high NH_3 volatilization from the Bladen soil. Water was added in

volumes that developed prolonged ponding in columns of this fine textured soil. During the period of ponding, NH_3 resulting from ureolysis (Eq. [1]) may have diffused into the liquid phase and volatilized therefrom. It is also possible that during ponding, unhydrolyzed urea diffused to the liquid phase and was deposited on the surface as the ponding gradually subsided. The negligible volatilization losses from both Plummer and Plummer + D under both soil moisture regimes seem to indicate that their high organic matter contents provided an adequate supply of protons to prevent NH_3 from being evolved (Eqs. [5a] and [5b]).

The low volatile loss of NH_3 detected in the acidified sorbers in Experiment 4 was probably due to the low laboratory temperature and short experimental period.

The budgets of N made in Experiments 2A and 2B (Tables 10, 11, 14, and 15) indicate that more N was left unaccounted for in the pots fertilized with urea than those fertilized with $(NH_4)_2SO_4$. In Experiment 2A, the control pots turned out a net gain of 95 mg N (0.021 x 4524 mg) and 194 mg N (0.045 x 4524 mg) per pot under the high and low soil moisture regimes, respectively. The amount of N (29 mg/pot apparently deposited by rainfall (Note, Table 10) on the pots was insufficient to account for such gain. It is possible that true N concentration in rainwater was not obtained, as each rainfall was not analyzed for N. Thick algal crusts were observed on the surface of the soil receiving no N addition. It has been estimated that algal crusts of desert soils may fix atmospheric N in the range of 4 to 84 g N/ha/hr (MacGregor and Johnson, 1971; Rychert and Skujins, 1974). Jensen (1965) reported a much higher fixing rate, 1000 to 1200 g/ha/hr. It is difficult to make any projection from these data because they were

obtained based on laboratory cultures. Nevertheless, these data indicate that presence of algal growth on the soil surface could account for N accretion in the soil. Underestimation of the residual N also may have contributed to the discrepancy in the N budget. The soil subsamples in Experiments 2A and 2B were air-dried. During the analysis of the soil samples in Experiment 3, it was found that total N in an air-dried sample was about 75 % of the undried samples. In fact, N lost during air-drying may help account for part of the item considered as N losses through volatilization and/or denitrification in the discussion that follows.

The items unaccounted for in Table 10 is expressed as percent of the added N(Table 11) and considered as gaseous losses through NH_3 volatilization and/or denitrification. These calculations of gaseous losses seem to be unrealistically high. The amount of N lost through the foliage that fell during the experimental period or through the severed rootlets during harvesting may have been considerable. Assuming that all pots uniformly lost N in this manner, results would still indicate higher gaseous losses of N from pots fertilized with urea than those unfertilized with N or those with $(NH_4)_2SO_4$. The N budget calculated in Experiment 2B indicated similar pattern of apparent gaseous losses with respect N treatments. One notable difference between the systems in Experiment 2A and 2B is that in the latter, there was no apparent gain of N observed in the control pots. This was probably because of shorter rainfall period, the seedlings in Experiment 2B were yet too young to shed matured needles, and their rootlets were not yet extensive at harvest time such that severance of rootlets was much less than in Experiment 2A. The higher loss of N apparently through volatilization from urea than with $(NH_4)_2SO_4$ ferti-

lization is reasonable considering the soil pH changes. Fig. 12 shows that within 2 weeks, leachate pH increased from 4.6 to 6.3 due to urea fertilization while it decreased from 4.6 to 3.4 due to $(NH_4)_2SO_4$ fertilization. This high leachate pH does not necessarily indicate the maximum pH attained in the soil, which has the potential to reach 11.0 around the urea granules (Fiskell, 1974, personal communication). It is highly possible that at discrete points in the soil, pH went higher than 7.7 such that protonation of NH_3 was minimized and loss through denitrification was maximized.

Nutrient Leaching

Losses of N

Leaching of N generally increases with fertilizer application rates, amount of water percolating through the soil, absence of growing crops in fallow soils, and in systems where downward flow of water (in lysimeters for example) is exaggerated (Brown, 1965). In Experiments 2A and 2B, leaching loss of NH_4-N* resulting from the addition of urea at a rate equivalent to 224 kg N/ha was not significantly different from the NH_4-N loss from the control pots (Tables 7D and 12C). When the rate of urea-N application was doubled, leaching loss of NH_4-N + urea-N significantly increased. The increase in leaching loss of NH_4-N due to increased urea-N rate was probably associated with two processes. One is the high leaching loss of unhydrolyzed urea-N which probably occurred because water was added before ureolysis was completed. The other is the possibility that the soil exchange sites were temporarily overloaded with cations (Thomas, 1970) and that root uptake was

*This includes unhydrolyzed urea-N detected in the leachates; 57.1 % and 49.5 % resulting from application rates of 224 and 448 kg N/ha as urea, respectively.

not sufficiently high to utilize all the available NH_4 ions. Leaching loss of NO_3-N was also significantly enhanced by urea fertilization at a rate equivalent to 448 kg N/ha. It is possible that NO_2-N constituted a considerable fraction of this N loss such that root uptake was further depressed through toxicity mechanism.

With regard to N source, Tables 7D and 12C indicate that NH_4-N losses due to urea fertilization were significantly less than the losses due to $(NH_4)_2SO_4$ fertilization. This was, again, associated with the low capacity of the soil to hold cations. Leachate pH went as low as 3.4 (Fig. 12) as a result of $(NH_4)_2SO_4$ fertilization, a process that further reduced the capacity of the soil to retain cations. On the other hand, leaching losses of NO_3-N were significantly higher with urea than $(NH_4)_2SO_4$ fertilization. The significant increase in acidity was probably detrimental to the activities of the nitrifiers. It is also possible that excessive leaching of NH_4-N restricted nitrification due to reduced available substrate. The low leaching losses of NH_4-N from pots fertilized with urea probably resulted from increased exchange sites brought about by pH rise.

The effect of soil moisture regimes was significant only on the leaching loss of NH_4-N (Table 7C). Although leachate volume was greater under the high than the low soil moisture regime (Table 17), leaching loss of NH_4-N was greater under the low moisture regime. Significantly higher N uptake under high than low soil moisture regime may have accounted for the difference in leaching loss of NH_4-N. The more or less identical sensitivity of nutrient uptake and leaching loss of NH_4-N to soil moisture conditions and the absence of significant effect of the latter on leaching loss of NO_3-N suggest that N uptake was mainly in the NH_4 form.

Table 17. Total amount of leachates collected from the lysimeter pots with two-year-old slash pine fertilized with urea and ammonium sulfate under two soil moisture regimes

N Fertilizer treatments[a]	Soil moisture regimes (cm of water) 170	500
	---------cm----------	
0	34.35	24.63
U1	33.58	21.56
S1	27.84	19.48
U2	25.23	20.54
S2	25.58	24.52

[a]N fertilizer treatments: 0 = no N added; U1 = N added as urea at rates equivalent to 224 kg/ha; S1 = N added as ammonium sulfate at rates equivalent to 224 kg/ha; U2 = 2 x U1; S2 = 2 x S1.

In Experiment 3, the effects of soil types and urea-N fertilization under two soil moisture regimes were evaluated. Leaching loss of NO_3-N was significantly affected by soil type; significantly higher amount of NO_3-N was detected in the leachate collected from the Bladen soil columns (Table 15G). Higher leaching losses of NO_3-N through the Bladen soil columns and greater KCl-extractable NO_3-N, which occurred under the high soil moisture regime (Table 16B2), seem to indicate that nitrifying activity was higher in this soil type than in the others tested. With the presence of more available NH_4-N to serve as nitrification substrate and less clay content to restrict water percolation, there should have been more nitrification and leaching of NO_3-N in the Plummer soil columns. Higher organic matter content (Buckman and Brady, 1969) and higher acidity in the Plummer soil (Table 1) and longer fallow period undergone by Bladen (the Bladen soil was stored dry for over a year while the Plummer soil was collected only two months before being used in the columns) may have accounted for the difference in nitrification and leaching losses of NO_3-N observed in Experiment 3.

Leaching losses of unhydrolyzed urea-N and NH_4-N were significantly affected by soil moisture regimes and urea fertilization (Table 16A). If the effect is evaluated in terms of the interaction between urea-N fertilization and soil moisture regimes, it can be found that the significant effect of the former occurred under the high soil moisture regime (Table 15B). Greater amount of urea-N was leached than NH_4-N (Tables 15B and 15F). This result strongly indicates that urea is highly susceptible to leaching when water is added before ureolysis is completed and that urea fertilization would only cause neglible leaching loss of N provided water is added after ureolysis is completed. Leach-

ing losses of N were dominated by unhydrolyzed urea-N under the high soil moisture regime. This underscores the importance of timing of water addition vis-a-vis stage of urea hydrolysis. That more NO_3-N was leached than NH_4-N under the high soil moisture regime seems to be consistent with the fact that soil colloids do not retain NO_3 ions.

Significantly more unhydrolyzed urea-N was leached from columns treated with PMA (Table 16F). On the other hand, PMA treatment slightly reduced leaching losses of NH_4-N and NO_3-N. The results would seem to indicate that PMA treatment did not only slow down ureolysis; it also reduced ammonification and nitrification activities. The reduction in the accumulation of NO_3-N was probably due to inhibition by PMA treatment or to lack of available NH_4-N as a substrate or to both.

Soil types exerted a distinct influence on the leaching loss of different forms of N (Table 16E). The ability of the soil to minimize leaching loss of unhydrolyzed urea-N appear to be associated with the organic matter content. Plummer soil with 20 % organic matter content (Table 1) allowed significantly less unhydrolyzed urea-N to be leached than either Leon or Bladen with organic matter content of 0.92 % and 2.75 %, respectively. Inclusion of debris in the Plummer soil samples further reduced significantly the amount of leachable urea-N. The low recovery of urea-N in the leachate and KCl-extractable fractions suggests that urea-N was incorporated in the soil in such a form that could possibly be detected through proximate method of determination as employed by Ogner (1972). Leaching loss of NH_4-N was significantly less from Bladen soil than from the other soil types. Low percolation rate through the Bladen column and low amount of KCl-extractable NH_4-N

probably were responsible for such result. Although leaching loss of NO_3-N was significantly higher from Leon than any of the other soil types, the values were generally negligible, ranging from 0.2 to 1.6 ppm, soil basis.

Timing of watering exerted a significant influence on leaching loss of urea-N only in the Leon soil where significantly more urea-N was leached out of the column when water was added 2 than 5 days after fertilization (Table 16C). These data would seem to indicate that conversion or incorporation of the added urea-N in other N forms occurred earlier in the Bladen and Plummer soils than in Leon.

Losses of Other Nutrients

Characterization of leaching losses of other nutrients was done in Experiments 2A and 2B (Table 7 and 12).

Urea fertilization apparently resulted in distinctly less leaching loss of P than $(NH_4)_2SO_4$ fertilization or where no N was added. Losses of P from the lysimeter pots not receiving any N treatment probably resulted from low P uptake by the slash pine seedlings. Low P uptake was probably a consequence of N deficiency. Leon soil has a very low P-retention capacity (Ballard, 1974) such that a considerable amount of P not taken up by the roots would easily move with the percolating water. The high leaching loss of P from pots receiving $(NH_4)_2SO_4$ certainly resulted from increased soil acidity. Although Udo and Uzu (1972) reported that P retention is usually negatively correlated with soil pH, low P retention is expected in a highly leached sand with very low Al and Fe content (Ballard, 1974). The ability of urea, therefore, to raise soil pH was advantageous in terms of minimizing leaching loss of P.

Leaching losses of K, Ca, and Mg in Experiments 2A and 2B were minimized by urea fertilization but enhanced by $(NH_4)_2SO_4$ fertilization (Table 7D and 12C). Higher uptake of these elements by the seedlings receiving urea treatment was, again, partly responsible for the lower leaching losses. On the other hand, the increased soil acidity due to $(NH_4)_2SO_4$ fertilization reduced the exchange sites available for the retention of such cations. The preponderance of NH_4 ions, which resulted from low plant uptake and low nitrification rate in the $(NH_4)_2SO_4$ fertilized pots, also displaced the K cations by mass action.

Although more water percolated through the soil under the high soil moisture regimes (Table 17), significantly less K was leached through such soil (Table 7C). By evaluating such K leaching variation in terms of the soil moisture regime-N treatment interaction (Table 7B), it can be seen that such high K leaching losses were associated with $(NH_4)_2SO_4$ fertilization. Although the minimum soil pH was observed in the high soil moisture regime (Fig. 12), it is possible that 2 to 5 weeks after fertilization, when moisture content of the soil under 500 cm of soil water tension was very low, effective concentration of H^+ was very high and the resulting high acidity probably enhanced the susceptibility of the added K to leaching. The same influence was not observed on Ca or Mg.

Mineralization

The mineralization process was measured by non-extractable and KCl-extractable N (Table 15F). The non-extractable N and KCl-extractable organic N were significantly reduced while the mineralized N components (NH_4-N and NO_3-N) were significantly increased by urea fertilization. The significant reduction of the non-extractable N in

Leon, Bladen, and Plummer + D soils resulting from urea fertilization appears to be a good indication of the ability of urea to promote the mineralization of organic N in the soil. The highest rate of mineralization appears to have occurred in the Leon soil, the lowest in the Plummer soil where urea fertilization did not significantly change the non-extractable N component. This type of variation may be explained in terms of C/N ratios. Broadbent and Nakashima (1965) showed that N reversion, the microbial conversion of available N into unavailable form, was generally enhanced by wider C/N ratios. The preponderance of energy supplied by soil organic matter would stimulate the N demand of the soil microorganisms. Using the information in Table 1, C/N ratios of Leon, Bladen, Plummer, and Plummer + D are 20, 19.7, 30, and 20, respectively. Reversion or immobilization appear to have occurred in the Plummer soil which had the widest C/N ratio.

Variation in KCl-extractable organic N with respect to N fertilization and soil type also followed the same pattern as the non-extractable N fraction. Since the value are expressed as percent of the total KCl-extractable N, it can be seen that urea fertilization shifted the distribution of the KCl-extractable N into mainly mineralized form. The data also indicate that the organic form of N in Leon was more easily extractable than those in the other soil types. The organic components in Leon soil were probably in more advanced stage of decomposition than those in the other soil types. The high clay content fo Bladen possibly held more closely the organic N compounds in similar mechanism reported by Greenland (1965) and therefore reduced the latter's KCl-extractability. In the case of Plummer and Plummer + D, the debris present in the latter probably contained more easily decomposable

compounds while the former may have contained organic compounds that were more resistant to decomposition and therefore less susceptible to KCl-extraction. Although mineralization rate was observed to be faster in Leon, the total NH_4-N mobilized by urea fertilization was less than the amount mobilized in the other soil types. This is undoubtedly a function of the total initial N content of the soil in which Leon has the lowest (Table 1). The variations in N distribution with respect to soil depths (Table 15H) further indicate that N conversion processes were more intense near the point of fertilizer application.

Regardless of soil moisture condition, the beneficial function derived from urea fertilization on these soil types is the mobilization of soil N into available form. The predominance of NH_4-N in the mineralized form (both KCl-extractable and leachable) suggest that ammonification is a predominant conversion pathway associated with urea fertilization.

Nutrient Retention

Retention of N

The amount of urea-N not leached by water but extractable by KCl varied by soil depth and soil types. Leon soil had the least capacity to retain unhydrolyzed urea-N (Table 16E). The Plummer soils held more unhydrolyzed urea than Leon soil apparently because of its high organic matter content which provided sufficient amount of organic compounds to form salts with urea (Broadbent and Lewis, 1964) and energy for biological immobilization. Retention of unhydrolyzed urea by Bladen was possibly a result of the compound adsorbed on the clay colloids through H bonding or ligand exchange (Mitsui, 1967;

Greenland, 1965). In Bladen and Plummer soils, more unhydrolyzed urea-N was retained in the lower portion of the column while the reverse was true in Plummer + D. Additional water would have flushed this out of the entire columns of Bladen and Plummer. In the case of Plummer + D, however, its high organic matter content seemed to have restricted the movement of unhydrolyzed urea-N.

The KCl-extractable NH_4-N and NO_3-N (Tables 15D, 15G, and 16E) suggest that retention of these N forms was a function of high organic matter or clay content. The influence of soil depths (Tables 15H and 16H) also indicates that high organic matter content of Plummer and Plummer + D and high clay content of Bladen were responsible for the slower movement of NH_4-N and NO_3-N in such soils than in Leon. Data on leaching losses of NH_4-N and NO_3-N (Tables 15B, 15G, 16B, 16E, and 16H) would seem to confirm the ability of such soils to restrict N movement. The slow mobility of NO_3-N was primarily due to the fact that nitrification in the systems investigated was low in the first place.

Retention of KCl-extractable and total N did not occur where potted slash pine probably depleted the N supply of the soil to a level that the nutrient became limiting long before the experiment was terminated. Another possible factor was the fact that the soil samples were air-dried. It was observed that total N in air-dried samples was only about 75% of that in undried samples. This process may partly account for the high amount of N that could not be accounted for in Experiment 2A (Tables 10 and 11).

Retention of Other Nutrients

Residual P, K, Ca, and Mg, evaluated at the end of a nine-month experimental period, indicate that more P was recovered in the pots subjected to a low soil moisture regime (Table 7C) or receiving addi-

tional N as urea (Table 7D). Under the high soil moisture regime, the amount of P recovered in the soil was essentially uniform for all N treatments while under the low soil moisture regime, more P was recovered in pots receiving urea-N treatment (Table 7B). Demand of P for growth of the potted slash pine, as indicated by higher P uptake under the high soil moisture regime (Table 7C) may have played a role on the depletion of P in the soil. Uptake of P by slash pine fertilized with urea was also high. Leaching loss of P, which was minimized by urea fertilization (Table 7D), mainly determined the final P status in the soil at the end of the experiment. Residual K and Ca were generally higher in pots fertilized with urea than with $(NH_4)_2SO_4$ (Table 7D). Considering the increased uptake and decreased leaching losses of nutrients the ability of urea fertilization in comparison to $(NH_4)_2SO_4$ fertilization to minimize leaching losses of K and Ca would seem responsible for the higher recovery of these nutrients in the urea fertilized pots. Recovery of Mg was essentially uniform in all pots regardless of soil moisture regimes or N treatments (Table 7A). This could be a result of soil Mg depletion by plant uptake and leaching losses.

Change in pH

Increase in soil pH was consistently observed with urea fertilization. Soil pH increased directly with levels of urea-N application and when soil moisture conditions were favorable for higher chemical and biological activities. In Leon soil, it was observed that urea-N applied at the rate of 236 ppm (Experiment 1) resulted in a maximim soil pH of 8.1 (Fig. 10). The potential pH at the very point of application is 11.0 (Fiskell, 1974; personal communication). Diffusion of OH ions from the alkaline pockets would account for a soil pH rise

below the potential and the extent and rate of such diffusion should be a function of the initial soil pH and buffering capacity of the soil. The effects of soil types with varying organic matter and clay content on soil pH would seem to bear this out. Highest maximum pH occurred in Leon, and lowest in Plummer, soils with low and high organic matter content, respectively. A lower pH rise occurred in Bladen than in Leon probably because in the latter a limited amount of organic acids was available to protonate NH_3 resulting from ureolysis, while a more abundant supply of protons was possible in the former. In Leon soil, the sources of protons were mainly the free acids or those occupying the exchange sites.

Rise in pH resulting from urea fertilization is temporary. Disappearance and/or complete protonation of NH_3 molecules, the decompostion of CO_3^{2-}, and oxidation of NH_4^+ ions in the process of nitrification are the processes that tend to bring soil pH back to its original level. Coincidence of pH drop with highest NO_3-N accumulation (Fig. 12) would seem to indicate a pH-nitrification relationship.

Slash Pine Growth Response

Urea at the rate of 448 kg N/ha elicited the largest response (Table 7D) by increasing height and diameter growth (15.6 cm and 7.7 mm, respectively) and total dry weight production (197 g). Neither level of N as $(NH_4)_2SO_4$ elicited any height growth response. The influence of $(NH_4)_2SO_4$ fertilization on diameter growth and dry weight production did not sharply differ from the influence of urea but in general, growth response to urea was better than to $(NH_4)_2SO_4$. The potted slash pine responded strongly to N fertilization under the high soil moisture regime.

All the growth measures positively correlated with nutrient uptake but negatively correlated with leaching losses of P, K, and Mg (Table 9). Interestingly, diameter growth and dry weight production were positively correlated with leaching loss of NO_3-N. This could be an experimental artifact but it is possible that the NO_3-N detected in the leachate included NO_2-N and the removal of the latter by leaching from the root zone may have removed the effect of NO_2 toxicity.

In general, higher nutrient uptake corresponded to greater growth with an exception in Ca uptake. Under the high soil moisture regime, Ca uptake was higher in pots fertilized with $(NH_4)_2SO_4$ than those fertilized with urea (Table 7B). Possibly, low pH and high moisture content promoted Ca solubility and consequently favored uptake or leaching.

Correlation between growth response and soluble salts was not apparent (Table 10). However, the seedling fertilized with $(NH_4)_2SO_4$ under the low soil moisture regime exhibited symptoms of salt injury; two seedlings eventually died. Considerably higher total soluble salts were removed through leaching from pots fertilized with $(NH_4)_2SO_4$ (Table 8). The differences in total soluble salts were probably reduced in distinctiveness by the essentially uniform amounts of soluble salts collected during the later part of the experimental period. Of particular interest is the extremely high amount of soluble salts (5.64 g) collected from the pots receiving 448 kg N/ha as $(NH_4)_2SO_4$ under the low soil moisture regime 65 days after fertilization. The time of collection was June 15, approximately within the most active part of the growing season. Prior to leaching, residence of such amount of soluble salts in the soil-root system under low moisture conditions

undoubtedly developed high concentrations of such salts, which may have been injurious to the roots. Bear (1942) reported that high concentrations of salts in the soil would cause root injury by plasmolysis, especially in sandy soils. High concentrations of soluble salts may also injure roots through the development of high osmotic pressure of the soil solution. This condition had been observed to reduce water absorption, increase leaf water deficits, and result in injury to tissues from dehydration on days when wind and high temperature cause rapid transpiration (Kramer and Kozlowski, 1960).

There was no growth response to N fertilization in Experiment 2B (Table 12A) possibly because the experiment was started in the middle of the growing season and leaching losses of N were excessive, as high as 95 % of the added N, from the pots fertilized with $(NH_4)_2SO_4$ (Table 12). High leaching losses of the other nutrients were excessive also. Leaching losses were probably enhanced by the use of cone-shaped lysimeter pots and by the fact that the soil was filled into the pots only two weeks before fertilization. In general, where slash pine growth was best, nutrient uptake was greatest and leaching losses were least.

SUMMARY AND CONCLUSIONS

A series of lysimeter, greenhouse, and laboratory experiments were conducted to determine the influence of soil moisture, soil organic matter and clay content, and rates of urea application on the trasformation and movement of urea in forest soils. The purpose of these tests was to characterize and understand the transformation pathways of urea-N applied to Southeastern Coastal Plain forest soils possessing various characteristics.

In an incubation experiment using a Leon fs, high rates of ureolysis and ammonification were observed under high soil moisture conditions. Keeping the soil too dry resulted in a considerable amount of unhydrolyzed urea that was detectable at the end of 42 days. Addition of PMA to the three forest soils before the uniform addition of 100 ppm urea-N resulted in high leaching losses of unhydrolyzed urea and low ammonification rate. Effectiveness of PMA as a urease inhibitor was greater in Leon fs than in Plummer fs, with organic matter content of 0.92 and 20 %, respectively.

In a greenhouse soil column experiment, additions of urea-N under two soil moisture regimes resulted in increased mineralization rates. Greatest rate was observed in Leon fs and the least in Plummer fs. Leaching losses of unhydrolyzed urea were more from soils maintained at high rather than at low soil moisture conditions. On the other hand, high rates of NH_3 volatilization were observed under low soil moisture conditions.

In a lysimeter experiment, potted slash pine received three levels of N from two sources, urea and $(NH_4)_2SO_4$, under two soil moisture regimes. Slash pine growth response was greater to urea under high soil moisture conditions, than to $(NH_4)_2SO_4$ under low soil moisture conditions. Leaching losses of nutrients were less from urea than from $(NH_4)_2SO_4$ fertilization. An accounting of the N distribution in the lysimeter system showed that urea and $(NH_4)_2SO_4$ fertilization resulted in slash pine uptake of 64 and 49 %, leaching losses of 17 and 51 %, and apparent gaseous losses of 19 and 0 % of the added N, respectively.

Nitrification was generally low under all conditions tested. Urea fertilization invariably caused soil pH to rise while $(NH_4)_2SO_4$ addition resulted in higher soil acidity.

From these results, it is concluded that:

(1) Urea was a better fertilizer than $(NH_4)_2SO_4$ for two-year-old slash pine, especially under high soil moisture conditions. Favorable growth response to urea fertilization was probably due to the rise in soil pH which may have favored better nutrient availability (Beaton, 1973), increased metabolic efficiency resulting from an increased supply of NH_4 ions, the possible uptake of unhydrolyzed urea and the products of ureolysis such as NH_3 and CO_3, and minimized leaching losses of nutrients. Relatively poor growth response to $(NH_4)_2SO_4$ fertilization was probably due to high concentrations of soluble salts and high leaching losses of nutrients.

(2) Keeping soil moisture conditions extremely low greatly reduced ureolytic activity. This underscores the essentiality of water in the process of ureolysis.

(3) The predominance of ammonification following addition of urea to the soil was observed. This seems to be beneficial for slash pine, a native tree species of the Southeastern Coastal Plain, which grows well with NH_4 as the main form of available N (Smith, 1972; personal communication).

(4) Because nitrification rate following treatment of the soil with urea was generally low, use of urea in forest fertilization does not seem to pose any danger of polluting the ground water with nitrates.

(5) Timing of water addition following urea fertilization was observed to be very important. While adding water too late or at insufficient amounts favored high volatile loss of NH_3, adding too much water soon after urea application promoted leaching loss of unhydrolyzed urea-N. It seems necessary that water be added such that urea molecules are removed from the volatilization zone but not out of the root zone.

(6) Although the soils used in this study were highly acid, high rate of volatile loss of NH_3 was observed. The volatilization aspect following addition of urea to the soil has been a widely investigated process. However, quantitative information still remains unreliable largely because of the shortcomings associated with each of the variety of methods of measuring evolved NH_3. Assessing NH_3 volatile loss by difference method (Nommik, 1973a) appears to be the most reliable.

(7) Although soil pH rise appeared to have a beneficial effect by increasing soil exchange sites to accommodate more cations, it may lead to denitrification losses of N. This possibility was a strong one in Leon fs where pH values reached as high as 8.1.

(8) Leaching loss of unhydrolyzed urea-N and volatile loss of NH_3 appeared to be minimized by high soil organic matter content.

However, a possibility of urea-N immobilization by the humus fraction was indicated.

APPENDIX

Table 18. Standard errors of the mean of parameters measured in Experiments 1 to 4

A. Experiment 1. Incubation

Parameters	Sources of variation			
	W (30)	T (40)	D (24)	WxT (10)
Urea-N (%)	1.56	1.37	1.77	2.74
NH_4-N (%)	1.14	0.98	1.27	1.97
NO_3-N (%)	0.42	0.36	0.46	0.72
Soil pH	0.12	0.10	0.13	0.20

W = soil moisture regimes; T = urea-N treatments; D = incubation periods. Values in parenthesis refer to the number of observations associated with each source of variation.

B. Experiment 2A. Lysimeter pots with two-year-old slash pine

Parameters	Sources of variation		
	W (20)	T (8)	WxT (4)
Growth response			
Height (cm)	0.81	1.29	1.82
Diameter (mm)	0.32	0.50	0.71
Dry weight (g)	8.40	13.29	18.79
Nutrient uptake (mg)			
N	44.44	70.27	99.38
P	7.70	12.18	12.22
K	16.10	25.46	36.01
Ca	24.78	39.18	55.40
Mg	8.30	13.12	18.56
Leaching losses			
NH_4-N (%)	0.57	0.90	1.27
NO_3-N (%)	0.12	0.19	0.28
P (mg)	12.60	19.92	28.17
K (mg)	14.06	22.23	31.44
Ca (mg)	28.74	44.44	64.27
Mg (mg)	9.94	15.71	22.22
Soluble salts (g)	0.22	0.35	0.50

Table 18. continued.

B. continued.

Parameters	Sources of variation		
	W (20)	T (8)	WxT (4)
Leachate pH			
1	0.07	0.11	0.16
2	0.12	0.18	0.26
3	0.13	0.20	0.28
Final soil pH	0.14	0.22	0.32
Residual nutrients			
N (ppm)	0.44	0.69	0.98
P (mg)	4.59	7.26	10.26
K (mg)	6.81	10.77	15.23
Ca (mg)	162.65	257.18	363.71
Mg (mg)	12.46	19.70	27.87

W = soil moisture regimes; T = N fertilizer treatments.

C. Experiment 2B. Lysimeter pots with one-year-old slash pine

Parameters	Sources of variation	
	DS (10)	NFT (4)
Growth response		
Diameter (mm)	0.64	1.02
Dry weight (g)	3.91	6.18
Nutrient uptake (mg)		
N	32.47	51.34
K	14.23	22.50
Mg	3.13	4.95
Leaching losses		
NH_4-N (%)	0.79	1.24
NO_3-N (%)	0.13	0.21
P (mg)	9.96	15.74
K (mg)	20.45	32.33
Ca (mg)	14.95	23.64
Mg (mg)	8.91	14.09

Table 18. continued.

C. continued.

Parameters	Sources of variation DS (10)	NFT (4)
Leachate pH		
1	0.22	0.36
3	0.11	0.18

DS = degree of shading; NFT.= N fertilizer treatments.

D. Experiment 3. Greenhouse soil columns

(1) Parameters involving volatile and leaching losses of N

Parameters	Sources of variation M(16)	N(16)	S(8)	MxN(8)	MxS(4)	NxS(4)
Volatile losses						
NH_3-N (%)	0.56	0.56	0.80	0.80	1.12	1.12
Leaching losses (%)						
Urea-N	0.13	0.13	0.19	0.19	0.27	0.27
NH_4-N	0.01	0.01	0.02	0.02	0.03	0.03
NO_3-N	0.03	0.03	0.04	0.04	0.06	0.06

(2) Parameters involving non-extractable and KCL-extractable N and soil pH

Parameters	Sources of variation M(48)	N(48)	S(24)	D(32)	MxN(24)	MxS(12)	NxS(12)
Non-ext. N (%)	1.00	1.00	1.41	1.22	1.41	1.99	1.99
KCl-ext. N							
NH_4-N (ppm)	23.42	23.42	33.13	28.69	33.13	46.85	46.85
NO_3-N (ppm)	1.36	1.36	1.92	1.67	1.92	2.72	2.72
Org. N (%)	1.89	1.89	2.67	2.31	2.67	3.77	3.77
Final soil pH	0.06	0.06	0.09	0.08	0.09	0.13	0.13

M = soil moisture regimes; N = urea-N treatments; S = soil types; D = soil depths.

Table 18. continued.

E. Experiment 4. Laboratory soil columns

(1) Parameters involving N leaching losses and leachate pH

Parameters	Sources of variation			
	S (8)	P (16)	ST (16)	SxP (4)
Leaching losses of N (%)				
Urea-N	4.26	3.01	3.01	6.02
NH_4-N	0.50	0.35	0.35	0.70
NO_3-N	0.02	0.01	0.01	0.03
Leachate pH	0.28	0.20	0.20	0.39

(2) Parameters involving KCl-extractable N and final soil pH

Parameters	Sources of variation				
	S (16)	P (32)	ST (32)	D (32)	SP (8)
KCl-extractable N (%)					
Urea-N	0.17	0.12	0.12	0.12	0.24
NH_4-N	0.45	0.32	0.32	0.32	0.64
NO_3-N	0.005	0.01	0.01	0.01	0.02
Final soil pH	0.17	0.12	0.12	0.12	0.24

S = soil types; P = phenylmercuric acetate (PMA); ST = sampling time; D = soil depth.

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BIOGRAPHICAL SKETCH

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Mr. Sarigumba is married to the former Natividad V. del Mundo and has two children, Edzel and Glenn.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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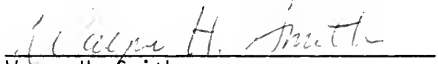

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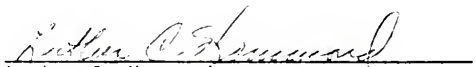

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